METEOR-Berichte

Geological setting, pore water chemistry, sediment chemistry, and metagenomics of hydrothermal systems in the Tyrrhenian Sea

Cruise No. M86/4

February 06 – February 20, 2012
Dubrovnik (Croatia) – Palma de Mallorca (Spain)

S. Petersen

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Editor:
DFG-Senatskommission für Ozeanographie
c/o MARUM – Zentrum für Marine Umweltwissenschaften
Universität Bremen
Leobener Strasse
28359 Bremen

Author:

Sven Petersen
GEOMAR Helmholtz Centre for Ocean Research Kiel
Wischhofstraße 1-3
24148 Kiel
GERMANY

Phone: +49 (0)431 600 2110
Fax: +49 (0)431 600 2924
E-Mail: spetersen@geomar.de

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Leitstelle Meteor / Maria S. Merian
Institut für Meereskunde — Telefon: +49 40 428 38 3974
Universität Hamburg — Telefax: +49 40 428 38 4644
Bundesstraße 53 — leitstelle@ifm.uni-hamburg.de
20146 Hamburg

Reederei F. Laeisz Bremerhaven GmbH — Telefon: +49 471 94549-19
Brückenstraße 25 — Telefax:
27568 Bremerhaven

Senatskommission für Ozeanographie
der Deutschen Forschungsgemeinschaft — Telefon: +49 421 218 65443
Vorsitzender / *Chairperson:* — Telefax: +49 421 218 65454
Prof. Dr. Michael Schultz — SeKom.Ozean@marum.de
MARUM Zentrum für Marine Umweltwissenschaften
Leobener Straße
28359 Bremen

Forschungsschiff / *Research Vessel* METEOR

Rufzeichen:	DBBH
Telefon-Nr.:	
InmarSat Fleet 77:	+870 76 165 1726
	+870 76 361 5079
Iridium:	+88 167 770 1858
GSM, Mobilfunk	+49 421 985 043 71
Telefax-Nr.:	
InmarSat Fleet 77:	+870 76 165 1728
	+870 76 361 5081
GSM, Mobilfunk	+49 421 985 043 79
E-Mail: (Schiffsleitung)	master@fs-meteor.de

1 Summary

The investigation of submarine hydrothermal systems in the Tyrrhenian Sea is generally aimed at a better understanding of the formation of submarine mineral deposits in island arcs where the shallow water depth (usually < 1000 m) and the influence of the subducting plate result in enrichments of gases, precious metals as well as abundant toxic elements at the seafloor. This cruise aimed at at a detailed mapping of known seafloor hydrothermal systems in an island arc setting using the autonomous underwater vehicle AUV "ABYSS". Due to the late arrival of the AUV in Europe from a previous cruise in the western Pacific, however, the AUV was not available for the cruise. This drastically affected the planned research. Instead of high-resolution AUV surveys, we used gravity coring along several transects over and beyond the mineralized area in order to sample the vertical extent of seafloor mineralization and to investigate the chemical variability of the overlying sediment. Overall 13 sediment cores were taken. The majority (N=10) was collected at Palinuro and many of these showed elevated temperatures within the core (up to 58°C) indicating that high-temperature fluids are far more widespread at Palinuro thean previously thaught. The patchy distribution of these "hot" cores indicates that upwelling of these fluids is likely fault-controlled in the subseafloor. The influence of magmatic degassing and microbial processes on pore water chemistry and its sulfur isotopic composition will be investigated on-shore using sediment cores with and without hydrothermal influence.

Geological sampling focused on two main areas, namely a known sulfide occurrence at the Palinuro volcanic complex and shallow marine sulfate deposits forming offshore Panarea Island. The study is continuing previous geological, geochemical, and biological work at these sites in the past couple of years using remotely operated vehicles (ROV's) and lander-type mobile drilling platforms during Poseidon cruises P340 and P412 as well as METEOR cruise M73/2. Additional sediment cores were collected from Glabro in order to evaluate the geochemical signature in this easternmost part of the Island Arc and to possibly detect geochemical signals of past hydrothermal influence away from the known vent sites.

Part of the shiptime was spent on collecting water column samples with the CTD-multirosette for analyzing the stoichiogenomics of microbial communities in seawater in order to trace the limiting affect of nitrogen on the genetic material of marine microbial communities along water depth gradients.

This sampling program was complemented by an extensive ship-based bathymetric mapping survey covering some 4700 km2 that were mapped using the Kongsberg Simrad EM122 multibeam system now providing a high-resolution map of the entire estern and northen part of the Aeolean Island Arc. We mainly used the EM120 to map volcanic edifices in the eastern part of the Aeolean Arc, however, the EM710 was used to map selected areas at the western summit of Palinuro in higher-resolution (10 m grid). A water column survey was obtained near Panarea in order to detect gas outlets associated with seafloor mineralization in the area.

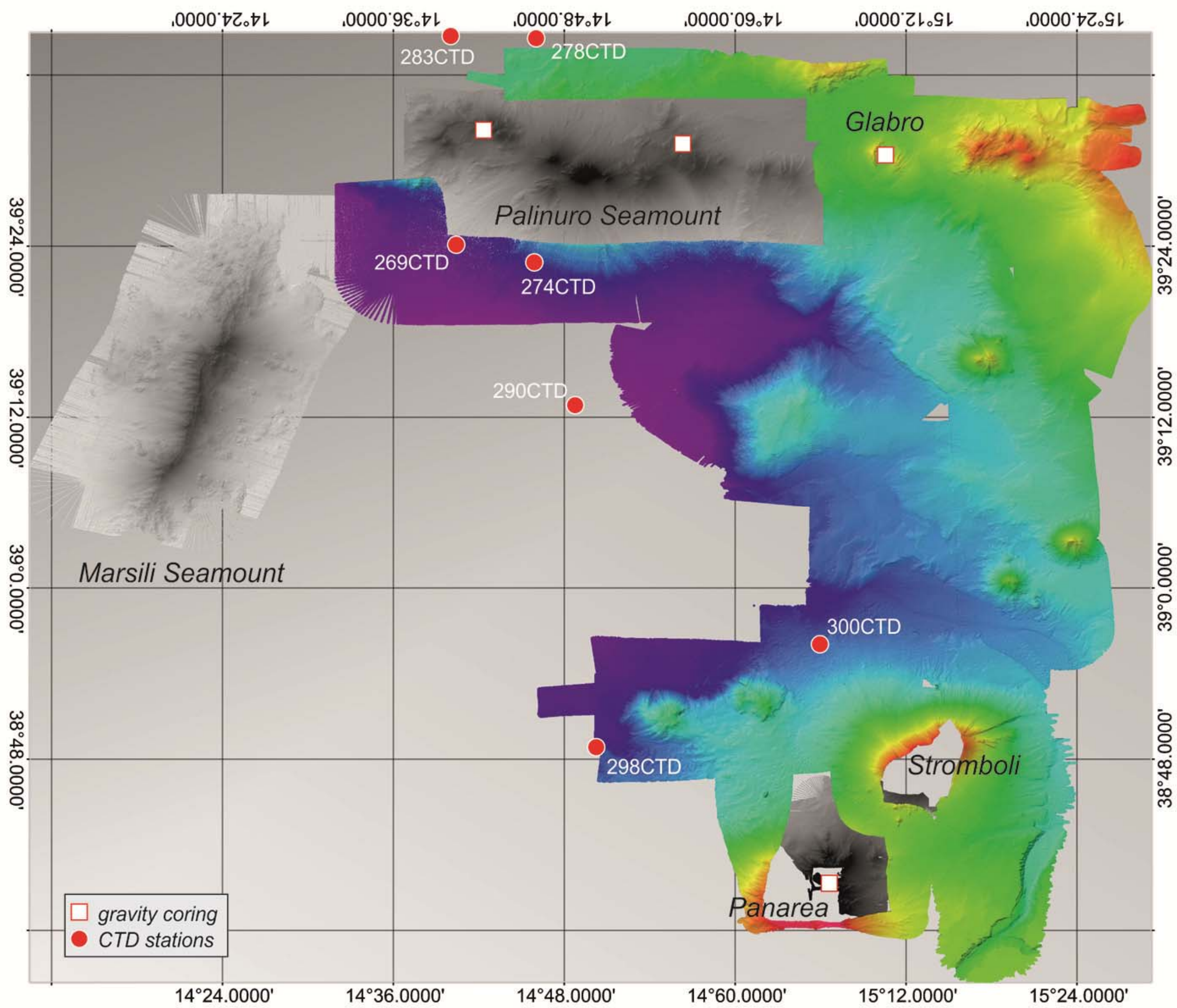

Fig. 1.1: Map of new bathymetry obtained during cruise M86/4 in the eastern part of the Aeolian Island Arc with location of CTD stations as well as areas where gravity corer stations were deployed. Bathymetry obtained during an earlier cruise is grey shaded (METEOR cruise M73/2 in 2007).

2. Participants

Name	Discipline	Institution
Petersen, Sven, Dr.	Marine Geology / Chief Scientist	GEOMAR
Augustin, Nico, Dr.	Bathymetry	GEOMAR
Wegmann, Kathrin	Bathymetry	GEOMAR
Garbe-Schönberg, Dieter, Dr.	Geochemistry	CAU Kiel
Berg, Bettina	Geochemistry	CAU Kiel
Chen, Xue-Gang	Geochemistry	CAU Kiel
Strauß, Harald, Prof.	Sulfur geochemistry	Uni Münster
Halama, Maximilian	Sulfur geochemistry	Uni Münster
Aqcuisti, Claudia, Prof.	Microbiology	Uni Münster
Meier, Dimitri	Microbiology	Uni Göttingen
Breuer, Christian	Geochemistry	Uni Bremen
Sahr, Paul-Jasper	Geochemistry	Uni Bremen
Crowhurst, Peter, Dr.	Structural geology	Nautilus
Hempelt, Juliane	Meteorologist	DWD
Raeke, Andreas	FW Technician	DWD

GEOMAR	Helmholtz-Centre for Ocean Research, Kiel
CAU Kiel	Christian-Albrechts Universität Kiel
Uni Münster	Westfälische Wilhelms-Universität Münster
Uni Göttingen	Georg-August Universität Göttingen
Uni Bremen	Universität Bremen
Nautilus	Nautilus Minerals Inc., Australia
DWD	Deutscher Wetterdienst, Geschäftsfeld Seeschiffahrt

3. Research Program

(S. Petersen)

This expedition was initially aimed at conducting detailed bathymetric mapping as well as sidescan and magnetic data acquisition of known shallow-water hydrothermal systems in the Aeolean Island Arc using GEOMAR's autonomous underwater vehicle AUV "ABYSS". These investigations aimed at a better understanding of the formation of submarine mineral deposits in island arcs where the shallow water depth (usually <1000 m) and the influence of the subducting plate result in enrichments of gases, precious metals as well as abundant toxic elements at the seafloor. These enrichments make such sites interesting from a resource point of view, but also because of the geogene input of toxic metals into the marine environment.

Cruise RV METEOR M86/4 aimed at answering the following questions:

- What geological structures host hydrothermal activity and its associated faunal communities at the two working sites?
- How widespread are faunal communities at Palinuro, and do they differ from those currently known?
- Is magmatic-hydrothermal activity at Palinuro focused on the western part or is there evidence for such activity in the underexplored eastern part of the volcano?
- How far does the known mineralization at Palinuro extent horizontally and vertically beneath the sediment cover and is the sediment thickness increasing away from the center of mineralization?
- What is the influence of ascending hot fluids and magmatic gases (SO_2, CO_2) on the chemical and sulfur-isotopic composition of the pore water?
- What is the influence of secondary microbial processes within the overlying sediments on the magmatic dominated sulfur cycle?
- What dimensions did gas eruptions in the vicinity of the Panarea islets have in the past and are such eruptions a future geohazard?

The focus of the cruise needed to be adjusted after the delay of the AUV and only those questions related to biology, magmatic input, and sediment distribution and geochemistry will be addressed with shore-based investigations. We were, on very short notice, able to invite Prof. C. Aquisti from the University of Münster to participate in the cruise. She is investigating the limiting affect of nitrogen on the genetic material of marine microbial communities along water depth gradients and was using the shipboard multirosette to obtain free-living microorganisms in water samples.

4 Narrative of the Cruise

(S. Petersen)

All scientific personnel arrived in Dubrovnik on February 05th and embarked the following morning. Dismantling the seismic equipment from the previous cruise continued during the day. A safety meeting was held at 14:20 UTC in the afternoon. R/V METEOR cruise M86/4 started at 17:00 UTC on February 06, 2012, when the vessel left the port of Dubrovnik (Croatia). METEOR headed for Ploce, the large container port north of Dubrovnik, in order to unload the scientific containers from the previous legs. We arrived at 07:00 UTC in the morning of February 07 at the pilot station, but were informed that we could not get into the harbor before afternoon. A scientific meeting was held in the afternoon. RV METEOR left Ploce again at 19:45 UTC and started its transit to the straight of Messina where we arrived on February 09, at 16:00 (UTC). During the transit a pressure low provided gusty winds and moderate waves. The transit time was used to set up the labs, to discuss the working plans of the various groups and for talks by various scientists on their latest research. R/V METEOR reached the working area shortly after 19:30 (UTC) on February 09. The scientific program started at 19:47 with a sound velocity profile (#267SVP) that was acquired prior to starting a bathymetric survey in the eastern part of the working area (#268MB) using the Kongsberg EM122 multibeam system. Mapping continued until the next morning (February 10) when a CTD/Multirosette was deployed southwest of Palinuro in order to sample surface, mid-water and bottom water for a metagenomic study and for associated nutrients and nitrogen analyses (#269CTD). A first gravity corer stations was targeted at the known area of hydrothermal activity near the western summit of Palinuro (#270GC) and recovered 3 m of sediment intercalated with porous sulfide layers and abundant native sulfur. The sediment temperature of 58°C at the base of the core indicates hydrothermal upflow in this area. Bathymetric mapping was conducted during the night despite heavy winds (8-9 Bft) and extended the coverage further to the N and NE of the Palinuro volcanic complex (#271MB).

On February 11, two gravity corer stations (#272GC and #273GC) were aimed at sampling the western limit of the hydrothermal activity at Palinuro. Core #272GC came up empty, but core 273GC recovered a full load of sediment. The temperature of 27°C at the bottom of the core indicates that this area is only weakly influenced by the hydrothermal upflow. Station #274CTD collected a second water column profile to the south of Palinuro and collected additional samples from bottom water, mid-water, and surface water for microbial studies. Another gravity core (#275GC) was deployed along the western flank of the mineralized summit, in an area where a previous dredge in 2006 recovered sulfidic material. The corer recovered homogeneous pelagic sediment. The nighttime was spent mapping the eastern extension of the Palinuro volcanic complex as well as Glabro Seamount in high-resolution (station #276MB).

The next two days (February 12 and 13) were used for sampling a series of gravity corer and CTD stations extending the survey area. Gravity corers were taken either within the mineralized area (#277GC, #285GC) or at selected promising targets to the east (#279GC, #282GC). Water samples for nutrients and metagenomic studies were collected to the NE (#278CTD) and NW of the western summit of Palinuro (#283CTD). The western summit of Palinuro hosting the known mineralization was mapped in high-resolution (10m) using the EM710 shallow water system (#280MB). Mapping was continued during the night and included mapping the area between Glabro, Alcioni and Lamentini (#281MB) as well as extending the survey area to the south of Palinuro (#286MB).

The first gravity corer on February 14 recovered hot sediments with sulfide crusts and native sulfur to the north of the hydrothermal active area at Palinuro (41°C; #287GC) and was supposed to be followed by a CTD cast in the Marsili Basin. Due to an instrument failure, the station was repeated (#290CTD). A second gravity corer tested the western extension of the mineralized area and recovered sulfide crusts but lacked the H_2S-smell and the presence of native sulfur seen in previous cores (#291GC). The night was spent mapping the southeastern part of Marsili Basin (#292MB) with a break for unwinding the cable on winch W3 due to the observed spin in the cable affecting CTD-work. Mapping continued while we moved to our second working area near Panarea.

In the morning of February 15 we approached the Central Islets of Panarea from the east and used the EM710/EM122 echosounding to map the distribution of gas venting to the north of Lisca Bianca on a single transect to obtain at least some information on the extent of gas venting in the area (#293MB), a task that would have been far better suited for the AUV “Abyss”. Two gravity cores were taken in a channel-like depression and recovered full loads of sediment (stations #294GC and #296GC) for pore water chemistry and sedimentology. Further mapping of gas venting between the cores and while leaving the Central Islets of Panarea at slow ships speed obtained water-column data from the echosounding systems (#295MB, #297MB). Strong winds prevented further gravity coring close to islands. Therefore we used station #298CTD to collect a water column profile to the west of Castore Seamount for microbial studies and their nutrient limitations.

Nighttime was used for mapping the area around Stromboli (#299MB) and on February 16 we deployed a final water colum station to the east of Castore Seamount for the metagenomic study (#300CTD). Due to the strong winds in the south we extended the bathymetric map of the eastern part of Marsili Basin and worked our way back to the north (#301MB) where we sampled the crater documented within Glabro Volcano using the gravity corer (#302GC) recovering background pelagic sediment. This station was followed by mapping of the northern extension of the Palinuro volcanic complex (#303MB) and a final gravity corer station testing the southern extent of hydrothermal acitivity at the western summit of Palinuro (#304GC).

Station work ended at 14:20 on February 17, 2012. During the transit to Palma de Mallorca the cable on winch W3 was again unspooled in order to establish its use during the next cruise. RV METEOR arrived in Palma de Mallorca in the morning of February 20, 2012. All equipment from M86/4 stayed on the vessel for the next Leg.

5 Preliminary Results

5.1 Multibeam bathymetric mapping

(N. Augustin, P. Crowhurst, K. Wegmann, S. Petersen)

During RV METEOR cruise M86/4 extensive multibeam mapping was carried out with hull mounted EM122 and EM710 echo sounder systems provided by Kongsberg Maritime AS. The EM122 multibeam echosounder collects bathymetric, corrected backscatter and water column imaging (WCI) deep water data over a wide swath to a maximum of 140 degrees (2 x 70°). The configuration installed on the RV METEOR operates in the 12 kHz frequency band in water depths up to >10,000 m. It has an across-ship swath with 864 soundings for each multi-ping. The EM710 multibeam echo sounder collects the same data packages as the EM122 in water depths of 2-2000m over a maximum swath width of 2 x 70°. It operates at sonar frequencies in the range of 70-100 kHz. It has an average across-track swath width of about 5.5 times the water depth. Data acquisition was conducted with Seafloor Information System (SIS) Version 3.8.3, Build 89 running in a Microsoft Windows 7 environment.

During METEOR cruise M86/4 approximately 117 hours and 1200 line km of multi beam data was collected. This created a new bathymetric dataset of 4,685 km^2 of the Tyrrhenian Sea between the coordinates: 38°36´N to 39°37´N and 14°12´E to 15°24´E. High resolution images covered many volcanic features such as Castore, Lametini, Alcioni and Glabro volcanoes, the base of Stromboli as well as large parts of the seafloor around them and the Marsilli Basin. Additionally, high-resolution EM710 data were collected from the western summit of Palinuro Seamount and CO_2 seeps at Panarea Island. The average ship speed during the bathymetric surveys was ~6 kn. During the EM710 surveys high-resolution seafloor data was collected at speeds of ~1-4 kn (Panarea, Palinuro respectively). The weather conditions were acceptable to good throughout the survey expect for one evening when rough sea conditions did not allow for good quality data to be collected (survey #271MB). Parts of this area were later resurveyed during survey #301MB.

The beam angle was set in SIS to automatic mode for most of the time, but manually limited when necessary (e.g., because of limited overlap of the mapped track lines). The Pingmode was also set to “Auto” because discrete manual settings like “Medium” or “Deep” did not result in better data quality. “Source Level”, “Pulse Length” and “Desired Ping Rate” were set to Automatic. To relieve the bottom detection for the system, we limited the search range manually and in case of need a “Force Depth” command was given until the bottom signal was found.

Area based editing of large parts of the collected data sets has been carried out using PFM files created by DMagic© as well as the 3D Editor modules included in the IVS 3D Fledermaus© Professional software package (Fig. 5.1). The IVS 3D FM Midwater module was used to evaluate the water column data and create images that visualize the extensive gas emanations from the seafloor at Panarea.

Final gridding and bathymetric map production was realized using the Fledermaus™ DMagic module. The data were gridded with a cell size of 25-30m for the EM122 data. Due to the good sea conditions during an EM710 water column survey at Panarea and the shallow water depth of this area, we were able to grid this data with a bin size of 1m.

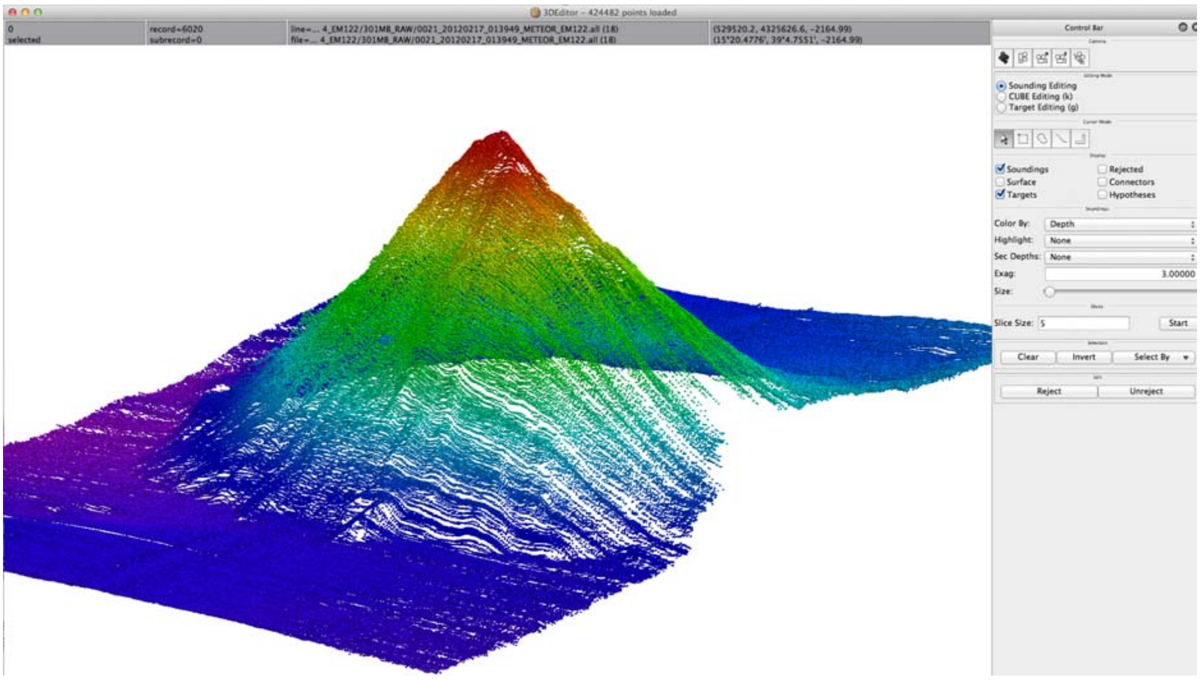

Fig. 5.1: Area based editing of a PFM file (Lametini volcano) with the 3D Editor, which is included in the IVS 3D Fledermaus package.

During M86/4 we collected good quality EM122 bathymetric data of the eastern Marsilli Basin, along the eastern sector of the Aeolian Volcanic Arc. The newly collected dataset extends the previous bathymetric mapped area of Marsilli and Palinuro Seamount, collected during METEOR cruise M73/2 in 2007.

The eastern Aeolian Arc extends from Panarea and Stromboli Islands to the Alcioni and Palinuro seamounts. Volcanism started at about 0.8 Ma and it is still active at Stromboli, partially around Panarea and the eastern seamounts (Soloviev et al., 1990). The working area is dominated by mainly three fault systems (Locardi and Nappi, 1979; Rossi et al., 1987). One is a NNE-SSW to NE-SW striking fault system, which affects the Stromboli and Panarea Islands. The Stromboli canyon (Fig. 5.2) has been interpreted as the surface expression of a NE-SW striking fault (Volpi et al., 1997).

Additional to the above-mentioned large volcanoes and volcanic complexes, a series of smaller volcanic features were covered as well (ie. Panarea, Stromboli, Glabro, Lametini, and Castore). As described by De Astis et al. (2003) NE-SW striking faults (minor N-S and NW-SE) are visible in almost all mapped subsea volcanic structures. The new high-resolution images created from this surevy revealed more detail in the local structures. Good examples come from Glabro and Alcioni at the NE rim of the Marsilli Basin (Fig. 3). Extensive crosscutting faulting has split these volcanoes apart. Particularly at Glabro, multiple episodes of faulting and partial rotation can be interpreted. The fault orientation is semi-parallel to the regional back-arc extension direction and creates a mini-graben feature with the inner section of the volcano collapsed with a central crater forming (Fig. 5.3). The arcuate fault pattern at Glabro mainly strikes NE-SW. At Alcioni volcano one NNW-SSE cross fault dips ~35° to SW. This fault is ~ 10 km long and splits the volcano almost symmetrically (Fig. 5.4).

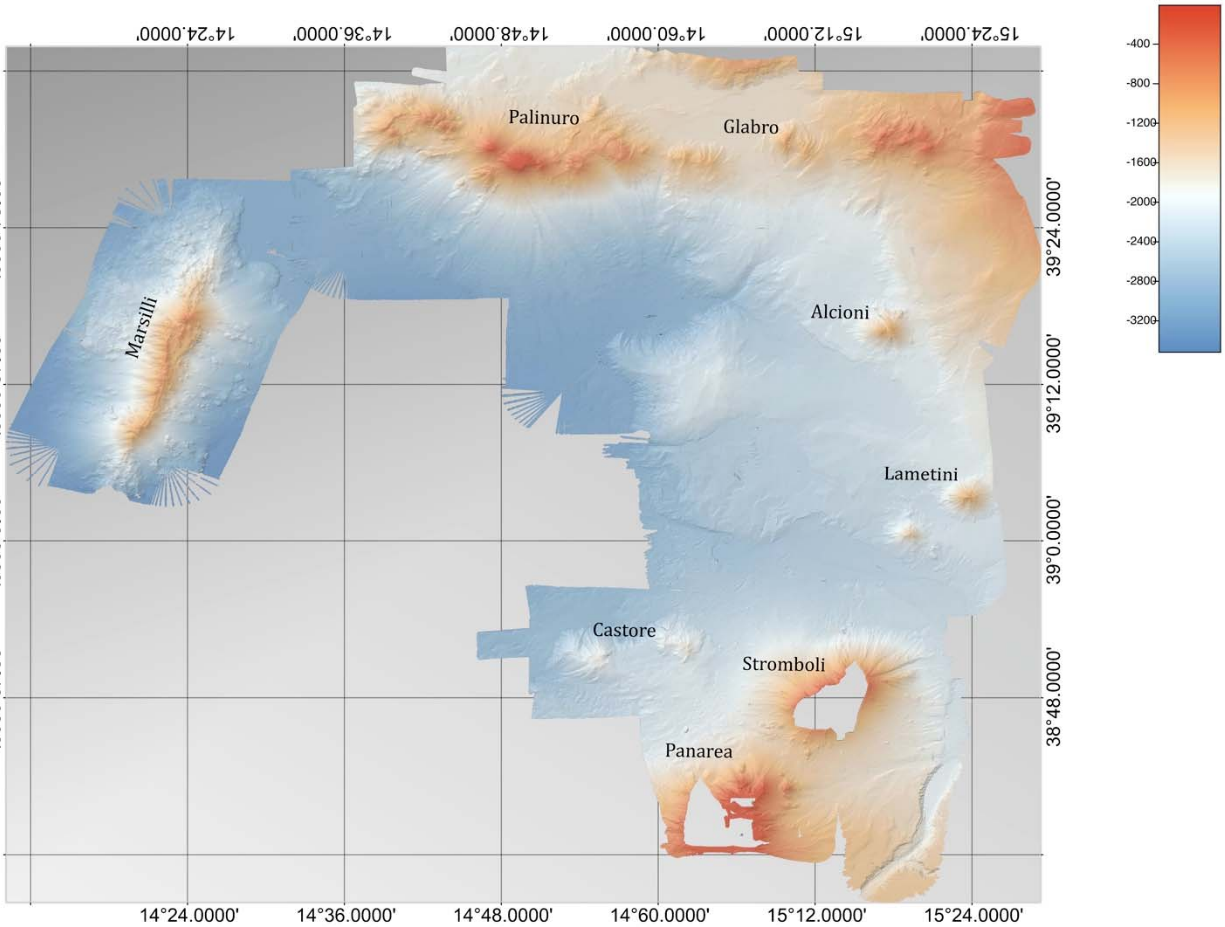

Fig. 5.2: Merged overview map of the survey areas of M73/2 and M86/4. The Marsilli and Palinuro seamount as well as parts around Panarea were previously mapped during cruise M73/2. During cruise M86/4 the gaps were closed and a broader area covered the northeastern volcanoes of Glabro, Alcioni, and Lametini as well as other regional features. The width of this map is ~115 km.

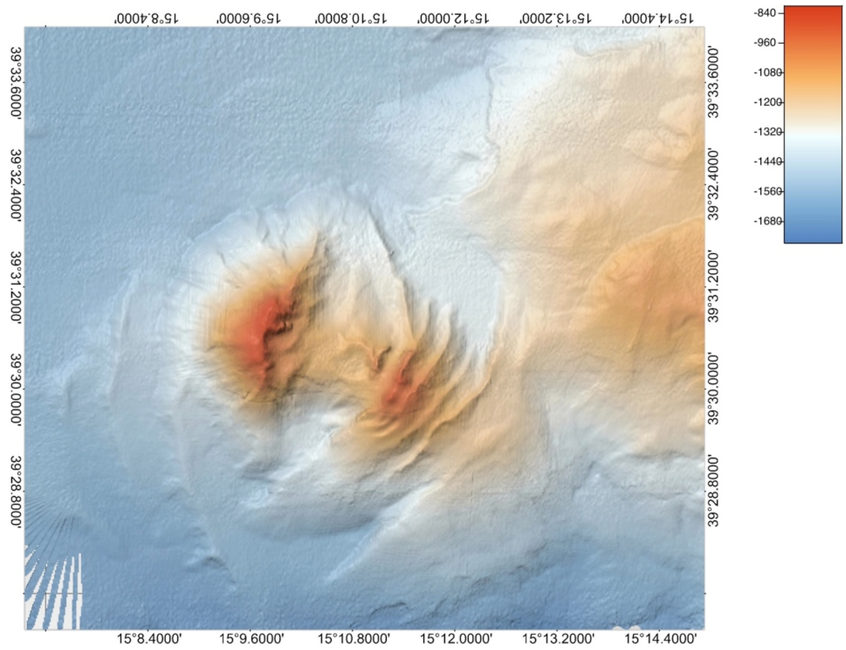

Fig. 5.3: Detail of Glabro Volcano, which is situated east of the Palinuro volcanic complex. Numerous NE-SW striking faults split the volcano, whereas a crater has been formed in the center of this structure. The base diameter of Glabro is about 6 km.

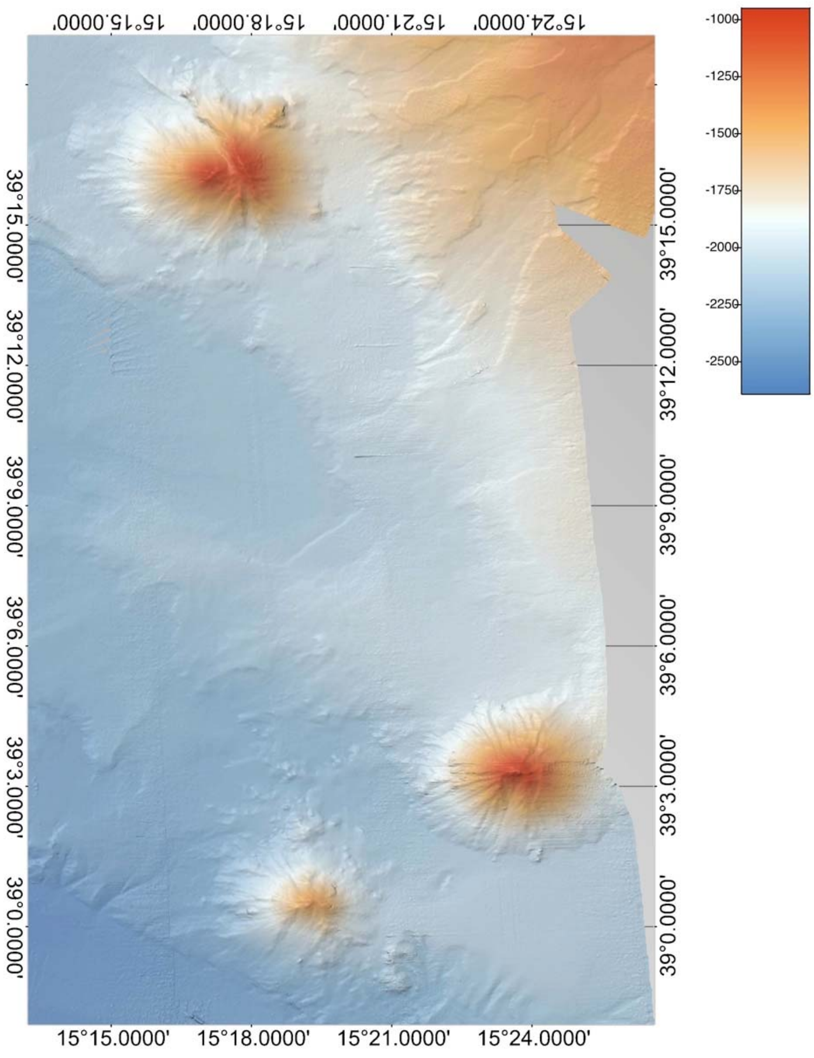

Fig. 5.4: Alcioni (north) and Lamentini Volcanoes (south) at the eastern rim of the Marsilli Basin. An arcute SW facing fault crosscuts the Alcioni volcano from NW-SE. The base diameter of Alcioni is about 8 km.

Complex, tectonic dissection is also visible at the Castore volcanoes west of Panarea and the western summit of the Palinuro volcanic complex, where most of the gravity corer stations during M86/4 as well as the Rockdrill drilling operations of M73/2 (2007) were conducted. Two V-shaped steep valleys split this structure into three segments, which are interpreted as the surface expression of main faults (Fig. 5.5). Hydrothermal activity and massive sulfide mineralization takes place in a crater like section on top the largest summit in the area. Another major fault in the western Palinuro complex is situated about 4.5 km west of the hydrothermal active zone and also strikes clearly NE-SW.

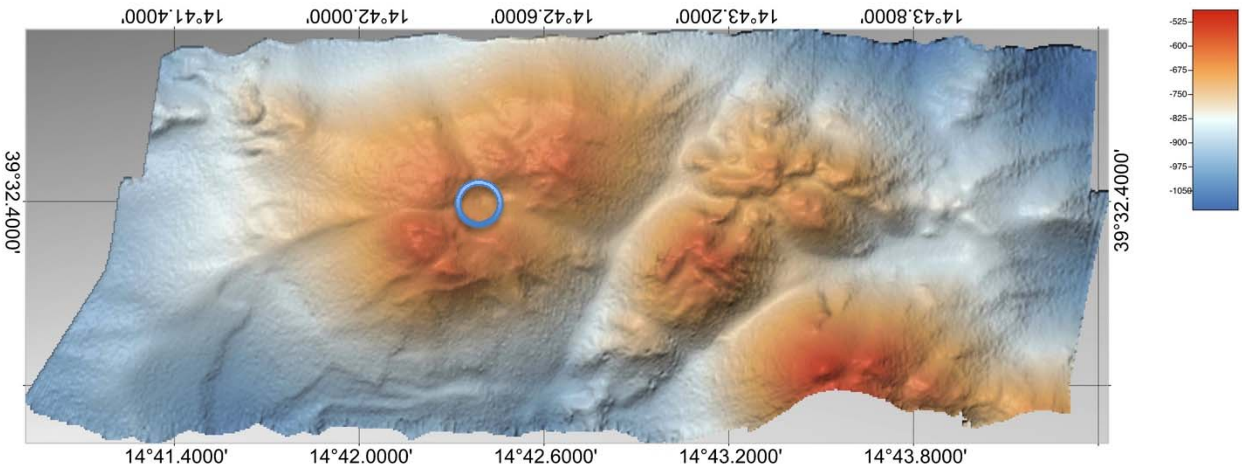

Fig. 5.5: EM710 bathymetry (Station 280MB) of the western summit of Palinuro volcanic complex. The model is gridded with a 10m bin size. The E-W extend of the map is 5 km. Most gravity coring (see chapter 4.4.2) was performed near the western summit of this structure (circle).

Overall the morphological and structural interpretation of the recent high-resolution bathymetry data clearly delineates the form of the volcanoes and allows for part of their history to be more clearly defined.

Water Column Data

During the multibeam surveys #293MB and #297MB we used the EM710 echosounder to collect water column data to image degassing from the seafloor close to Panarea and Basiluzzo islands. To collect good quality water column data the ship speed was slowed to 1 knot. Due to adverse weather conditions with a strong wind from the WSW, the heading of each track was 270° to avoid heavy interferences in the water column data produced by the bow thrusters. The data were preliminary processed in FM Midwater. Therefore the Kongsberg WCD data format needed to be converted into the Midwaters own WCI file format. Due to some software bugs in the Mac OS version of the FM Midwater module as well as instabilities under a Windows 7 environment we could not evaluate the data in all details during the expedition. However, the data quality seems to be good so far and preliminary imaging shows a multitude of clear signals in the water column, which reflect the degassing offshore Panarea. Figure 7 shows the flares of the degassing as a stacked image of all beams. The stacked view takes all of the beams in the swath and collapses them down together in an overlapped manner to display the maximum signal level for every discrete range increment. This image is not geometrically correct and is intentionally distorted to show as many of the water column features as possible.

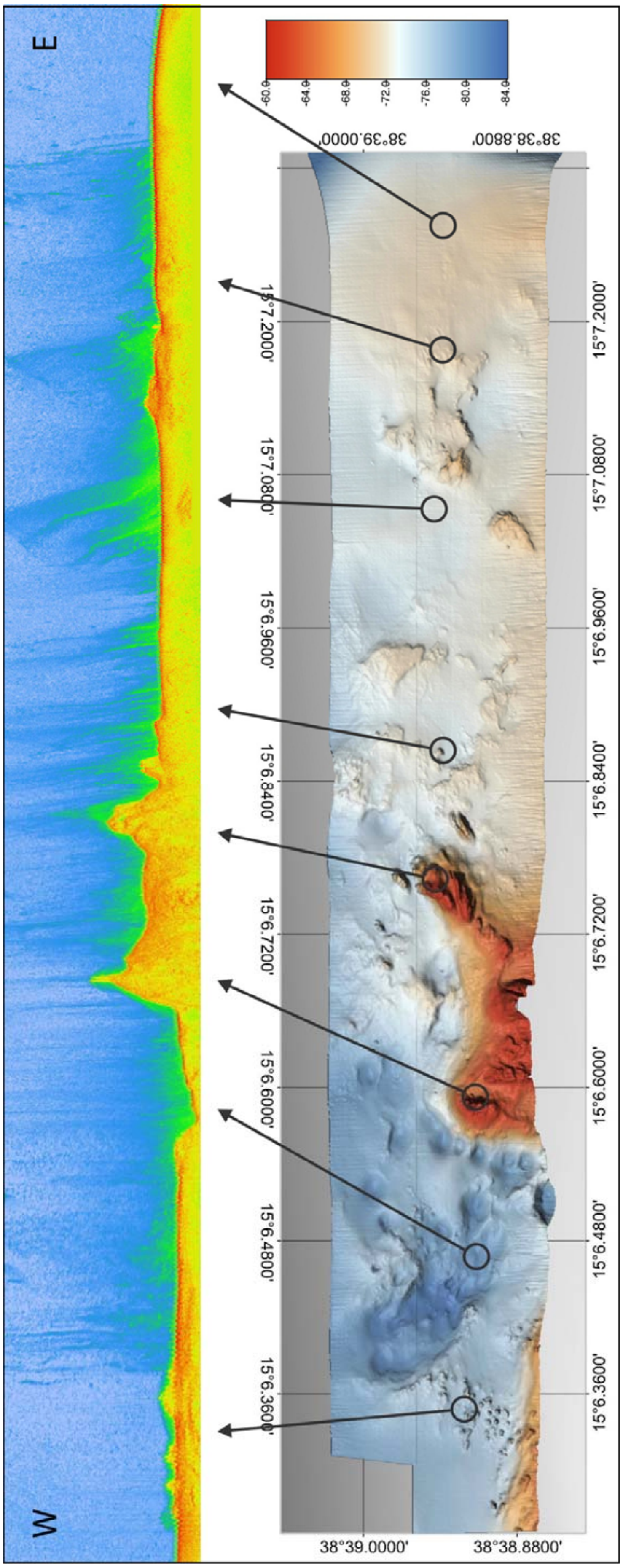

Fig. 5.6: Water Coloumn Data (WCD) shown in FM Midwater stacked mode for the surveyed area at Panarea, south of Basiluzzo Island. This view is not geometrically corrected. For details see text. Arrows point to structures at the seafloor seen in high resolution EM710 data gridded with a cell size of 1m.

5.2 Gravity Coring

(H. Strauss, M. Halama, D. Garbe-Schönberg, B. Berg, X.-G. Chen, C. Breuer, and P.-J. Sahr)

5.2.1 Sediment and pore fluid sampling

Overall 13 gravity corer stations (3m length, 125mm diameter, 600kg weight on top; Fig. 5.7) recovered sediment from various areas of the Tyrrhenian Sea. Most stations (10) were targeted in an area of known seafloor mineralization at the western summit of the Palinuro volcanic complex. The sediment cores here range in length from 40 to 300cm with recoveries typically 2.2-3 m, but only 0.4 m in some background pelagic sediments. Two additional deployments were unsuccessful. At Panarea two sediment cores were recovered with lengths of 290 and 300cm, respectively. One sediment core was collected at a crater-like depression of the Glabro volcanic structure and sampled a total length of 290cm of sediment.

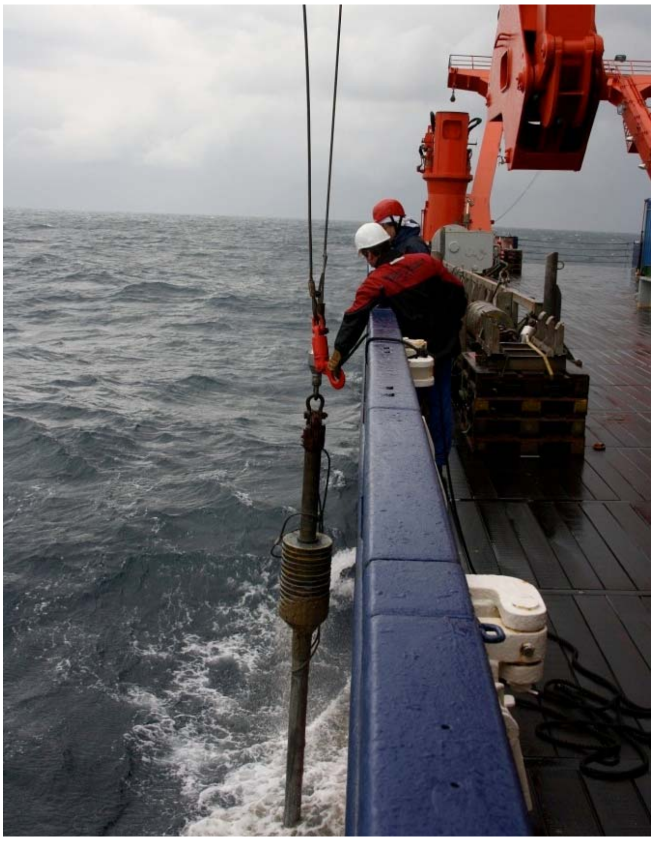

Fig. 5.7: Sediment sampling with the gravity corer

Upon recovery, the liners (125mm diameter) were cut into 1m long sections and the ends were sealed with lids. Holes were drilled into the liners at selected intervals in order to obtain pore water samples using Rhizon Soil Moisture samplers (Fig. 5.8). These samplers consist of a small microporous polymer tube (0.1 µm pore size) that is supported by a stabilizing glass fiber wire and connected to a PVC tube (Seeberg-Elverfeldt et al., 2005). The pore water was recovered using negative pressure produced by the attached 10ml syringes (Luer-Lock connection). Small dead volume (<0.5 ml) allows sampling of very small volumes of pore water. The applied method permitted extraction of the pore water with minimal disturbance of the sediment. Oxidation of pore water samples by air was minimized by connecting the Rhizon soil moisture samplers to syringes before the core section was opened.

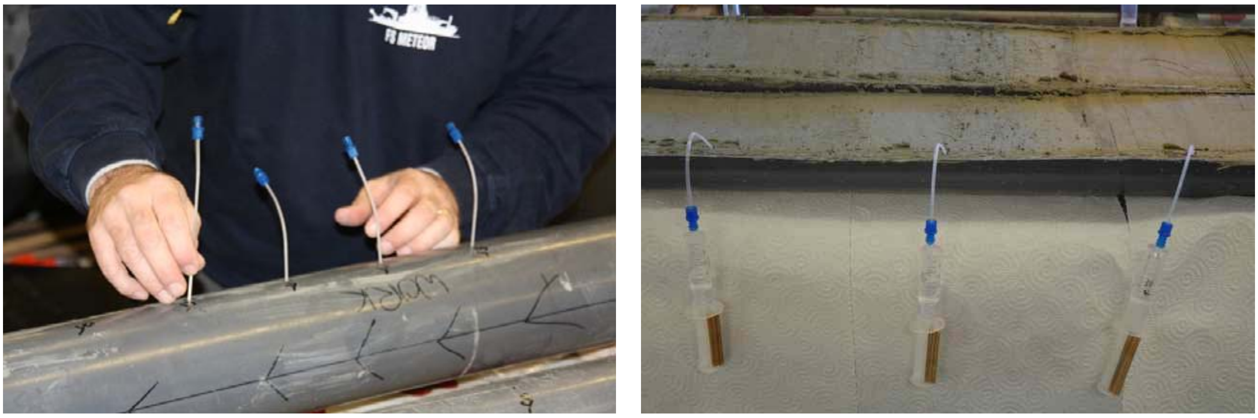

Fig. 5.8: Pore water sampling using rhizon soil moisture samplers

Pore waters were subsampled for on-board measurements of pH and dissolved sulfide concentration (see Appendix Table A1 for data). Subsequent to pore water sampling, the cores were opened using a hand-held vibro-cutter, and a lithological description was made (see Appendix 2). Sediment samples were collected for geochemical (Table A2; Appendix 1) and isotopic studies from the working half. One half core remained undisturbed as archive half.

Table 1: Overview of gravity coring (GC) stations obtained during M86/4.

Station	Latitude	Longitude	Water depth	Tmax	Recovery	Description
Palinuro						
270GC	39°32.400'N	14°42.378'E	633 m	58.0°C	242 cm	altered volcaniclastic sediment with 2 sulfide-rich layers + native sulfur in upper 70 cm; H_2S smell.
272GC	39°32.399'N	14°42.370'E	630 m	-	empty	no core recovery
273GC	39°32.401'N	14°42.385'E	628 m	26.8°C	300 cm	altered volcaniclastic sediment with numerous sulfide-rich layers, minor sulfur, vertical channel/ cast with Fe-stained sediments, H_2S, metalliferous sed.
275GC	39°32.201'N	14°41.949'E	725 m	-	40 cm	normal pelagic sediment, dark yellowish orange, homogenous.
277GC	39°32.410'N	14°42.404'E	638 m	39.0°C	300 cm	altered volcaniclastic sediment with coarse lapilli/ volcaniclastics layer, 2 sulfide layers, sulfur in layers/ crusts, S°-rich, top sediment missing, H_2S smell.
279GC	39°31.394'N	14°43.836'E	883 m	13.2°C	275 cm	normal pelagic sediment, moderate yellowish brown, shell fragments
282GC	39°30.598'N	14°56.303'E	802 m	13.2°C	40 cm	normal pelagic sediments, dark yellowish orange, black spots, volcanic ash fragments
285GC	39°32.411'N	14°42.385'E	629 m	38.1°C	285 cm	altered volcaniclastic sediment with oxi-dized top layer, 1 thick 35 cm sulfide layer, silica/sulfur crusts, spotty sulfur-rich; H_2S smell
287GC	39°32.437'N	14°42.390'E	623 m	40.6°C	242 cm	altered volcani-clastic sediment with numerous layers of sulfide-crusts (sulfide layers), alternating w/ S° sulfur rich sediment silica crusts, H_2S smell
291GC	39°32.410'N	14°42.371'E	625 m	19.1°C	237 cm	altered volcaniclastic sediment with numerous layers of sulfide crusts, silica crusts with orpiment (As-sulfide), top sediment missing, no H_2S!
304GC	39°32.379'N	14°42.370'E	628 m	15.4°C	225 cm	fully oxidized; mineralized, altered volcaniclastic sediment, numerous layers with oxidized sulfide crusts, massive silica crusts, no H_2S
Panarea						
294GC	38°38.956'N	15°06.395'E	75 m	20.0°C	220 cm	altered (?) tuffaceous sediment, degassing, silty/ sandy, plant detritus?, clay-rich layers, no H_2S
296GC	38°38.942'N	15°06.422'E	76 m	23.6°C	240 cm	bluish white, clay-rich sediment, pyrite-impregnated, argillic alteration of dacitic(?) tephra; coarse sand layer with mussel shell fragments in 25 cm, no H_2S
Glabro						
302GC	39°30.399'N	15°10.801'E	1112 m	13.4°C	290 cm	normal pelagic sediment, abundant shells/ tests, clay-silty, 45 cm oxidized top

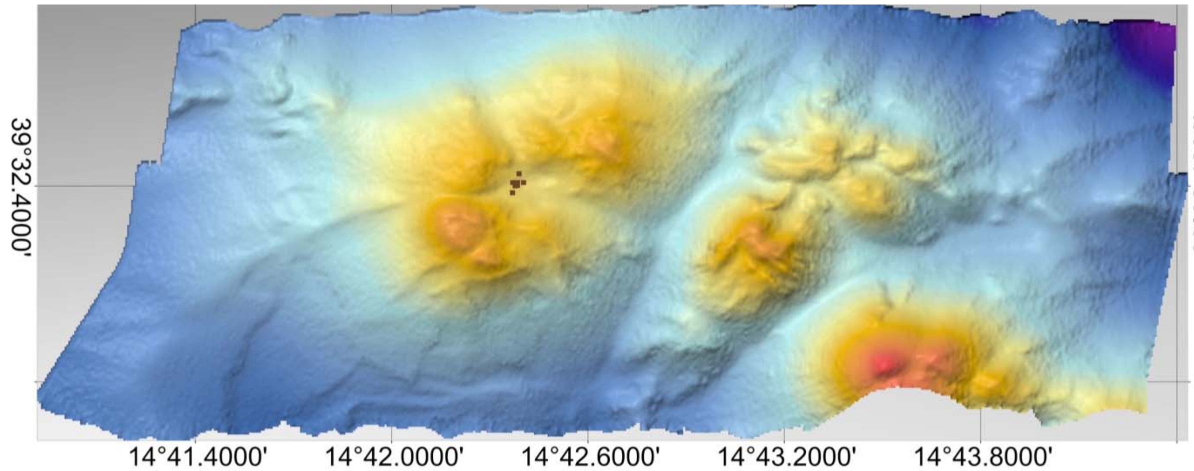

Fig. 5.9: High-resolution bathymetric map (EM710; 10 m grid) with location of gravity cores taken along transects over the mineralized area at the western summit of the Palinuro volcanic complex.

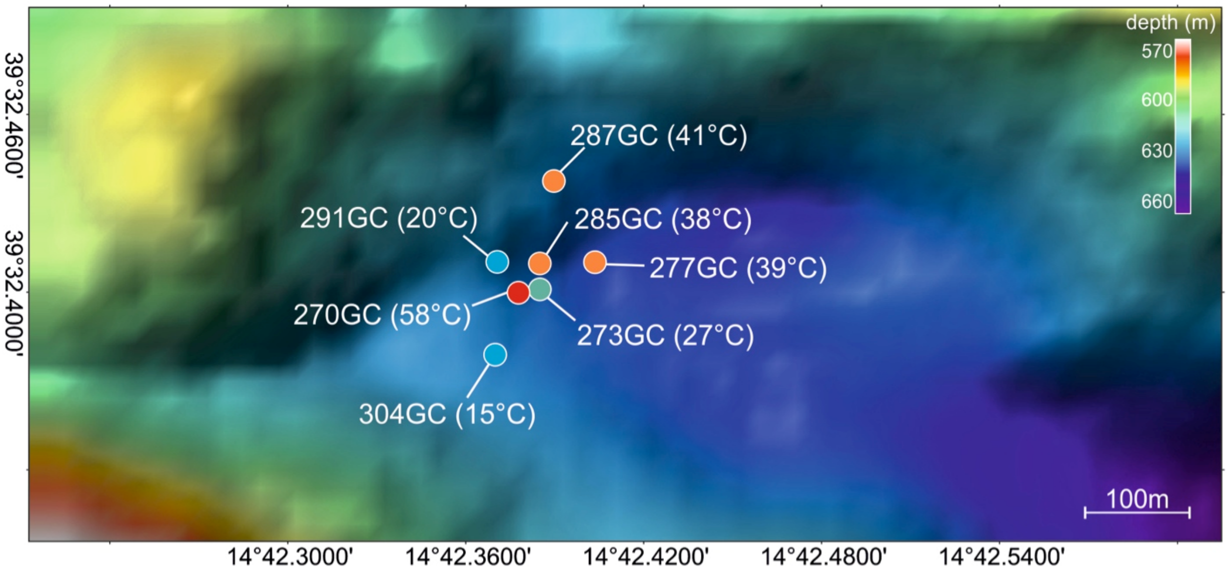

Fig. 5.10: Close-up of the summit with location of gravity cores recovered during M86/4. Colored symbols and temperatures recorded after recovery (in brackets) indicate the heterogeneous distribution of upwelling hydrothermal fluids.

5.2.2 Sediment description

The top region of a volcanic edifice in the western part of the **Palinuro** volcanic complex at about 630 m water depth is mineralized with massive sulfides. Previous work during cruises *Poseidon P340* (2006), *METEOR M73/2* (2007), and *Poseidon P412* (2011) characterized the general geological setting, mineralization style and geometric measures of the ore body by means of ROV observations, gravity coring and rock drilling. The objective of cruise M86/4 was to assess compositional and geochemical gradients across the mineralization and into the overlying sediment in more detail using 3m gravity coring into surficial sediments. In general, the study area exhibits fine-grained volcaniclastic/tuffaceous sediment with abundant lapilli-sized clasts. Sediments have undergone extensive hydrothermal alteration leading to a greenish-grey, clay-silty sediment with dusky green (?nontronite) spots and clasts. Pumice textures are still discernible in larger fragments. Intercalated in this sediment are dark grey to black, fluid-rich layers of both variable thickness (5 - 40cm) and number (1 to >7), with fragments of sulfide crusts and aggregates of elemental sulfur. Silica crusts, some with orpiment (arsenic sulfide) impregnation (Fig. 10), are abundant.

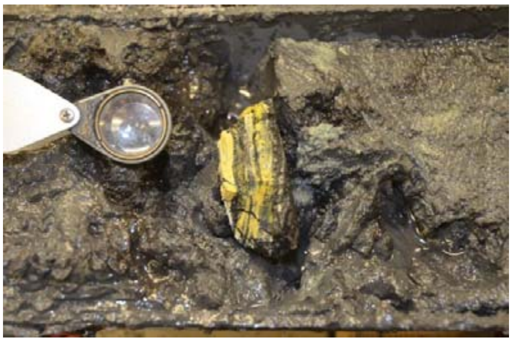

Fig 5.11: Silica-crust with disseminated yellowish orpiment (291GC, split core)

Five "hot" cores (#270GC, #273GC, #277GC, #285GC, #287GC) (Table 1) were recovered with an elevated sediment temperature ranging from 26.8°C – 58.0°C as measured after recovery on-deck in the core catcher. This compares to 13.2°C in ambient bottom water. The high sediment temperatures are indicative for a hydrothermal system with active fluid flow. All "hot" cores from this active hydrothermal area show pH values (5.8 – 6.4) lower than seawater and high dissolved H_2S concentrations (1.4 – 3.5mM H_2S) in pore fluids and are further characterized by disseminated sulfur globules and aggregates in altered volcaniclastic sediment adjacent to sulfide layers. Other cores with lower temperatures define a gradient from the "hot" hydrothermally active area towards cooler sites (#291GC) and, finally, to a fully oxidized core (#304GC). Two stations were used for exploration and sampling regional background pelagic sediment (#279GC, #282GC). Detailed sediment logs and core descriptions can be found in Appendix 2, and the following text gives brief summaries for each coring station (c.f., Table 1, Fig. 5.10).

The core from station #270GC was the hottest one during this cruise, having a temperature of 58°C in the core catcher. It contained mineralized, altered greenish volcaniclastic sediment and in the upper 70cm two black layers with sulfide crusts and elemental sulfur. The core was rich in disseminated elemental sulfur and had a strong H2S odor. Station #273GC was close to #270GC and recovered the same type of sediment but much cooler (26.8°C) and with an oxidized core top still in place. Another feature of this core is a vertical flute cast with FeOOH. Station #**275GC** was located on the outer SW slope of the volcanic edifice and sampled normal, homogeneous pelagic sediment of yellowish orange colour. The recovery, however, was only 40cm. Station #**277GC** continued the profile in line with #270GC, #273GC towards NE and sampled again mineralized, altered volcaniclastic sediment with numerous layers of sulfide and massive sulfur crusts. The sediment was rich in elemental sulfur and had a strong H_2S odor. Another background station E of the mineralized area was #**279GC**, sampling homogeneous pelagic sediment of moderate yellowish brown colour and with shell fragments and a piece of coral. Station #**282GC** was on the outer NW slope of the edifice in homogeneous pelagic sediment of dark yellowish orange colour showing numerous black coloured spots. The following two stations #**285GC** and #**287GC** located in the mineralized area recovered sediments that were still warm (38.1°C and 40.0°C) when the cores were opened on-deck.

The mineralized and altered volcanoclastic sediments have intercalated layers with sulfide, massive silica and sulfur crusts and are rich in disseminated elemental sulfur and H_2S, similar to those sampled with gravity cores #270GC, #273GC, and #277GC.

While core #285GC exhibits just one massive layer (35cm) of sulfide crusts, #287GC displays numerous sulfide layers that alternate with volcanoclastic sediment that is strongly impregnated with sulfur globules and aggregates. In principle, sediments in core #**291GC** are very similar to #287GC etc. but showed a low temperature (20.0°C) and no or very low dissolved H_2S in the pore fluid indicating that advection of hydrothermal fluid has ceased in this area. Interestingly, the top 30cm of the core comprise coarse sulfide crusts that presumably represent slumped sediment on top of the original, oxidized sediment surface. The highlight was a find of an entire 5 cm tall hydrothermal chimney (?) or pipe and a few burrows, now being partly oxidized to FeOOH (Fig. 5.12). Another interesting feature of this core was the occurrence of a massive (3 cm) silica crust with yellowish orpiment (arsenic sulfide) impreg-nation (c.f., Fig. 5.11). How surficial mineralized sediment will change if this condition of ceased hydrothermal activity prevails for longer time periods can be studied in the southernmost core sampled during this cruise at station #**304GC**: the original texture of the mineralized and altered volcanoclastic sediment with numerous layers of former sulfide crusts, massive silica and sulfur aggregates is still clearly visible but oxidation from percolating seawater converted disseminated pyrite and iron sulfide crusts into massive FeOOH.

Fig. 5.12: Oxidized hydrothermal sulfide crusts and burrow-fillings from sediment top (#291GC).

PANAREA. The geological setting of this study area offshore the volcanic island of Panarea is different in many respects when compared to Palinuro. Widespread volcanic degassing is observed in shallow water depths of ≈80 m water depth driving argillic alteration of andesitic to dacitic volcanoclastic sedimentary deposits. Fluid only slightly warmer (< T ≈1°C) than ambient seawater is seeping from the seafloor along fissures creating suboxic to anoxic micro-environments. The mineralization comprises disseminated (3-5%) pyrite. The research objective for this area was complementary sampling of sediment cores and pore fluids in order to strengthen the weak database from this area. Two cores were taken from a depression that was presumably formed by a large subaquatic gas eruption. Station #294GC sampled brownish, altered tuffaceous sediment of silty/sandy grain size and with thin carbon-rich layers from plant detritus. Intercalated are more clayey layers. There was no H2S detectable. The core was heavily degassing upon retrieval. The second core, #296GC, contained more or less uniform homogeneous bluish-white clayey sediment (?montmorillonite/alunite) with pyrite impregnation. At 25cm depth, the sediment is composed of a coarse sand layer with mussel shell fragments. No H_2S was detectable in the pore waters.

Finally, the Glabro volcanic complex was explored with one single station #302GC retrieving normal pelagic, clayey-silty sediment with abundant shell fragments, biological tests etc. The top 45 cm were oxidized.

5.2.3 Major and trace element geochemistry at Palinuro and Panarea
(D. Garbe-Schönberg, B. Berg, X.-G. Chen)

The two study areas at Palinuro and Panarea are characterized by extensive sub-seafloor sulphide mineralization of hydrothermal origin. Mineralizing hydrothermal fluids transport heat and dissolved metals, ligands, gases, and other components during, and after, intense reaction of heated seawater with host rocks (here, mainly island arc volcanic rocks and volcaniclastic sediments). In addition, magmatic degassing is believed to be a source for direct addition of volatiles like e.g., CO_2, SO_2/ H_2S, As, Hg and other metals. Mixing of the hot, acidic, and reducing hydrothermal fluid with ambient seawater leads to precipitation of insoluble compounds (e.g., sulphides, anhydrite, baryte, native sulphur) either at, or below, the seafloor. More soluble compounds (e.g., As species, Tl, Pb, Hg, alkali elements, nutrients, dissolved gases) are dispersed from small seeps and vents into the bottom water.

Our results from cruise POS412 in 2011 show that Palinuro hydrothermal (pore) fluids are characterized by extreme concentrations of alkali elements and very high Si, Ca, Sr, and As, Sb, W. The hydrothermal endmember composition of these fluids is that of a brine with almost twice seawater salinity. In contrast, Panarea fluids have very high concentrations of heavy metals like Pb, Tl, Ag, Zn, and As, Sb. Here, fluids show also elevated salinity but a co-variation of highly enriched alkali elements with Mg concentration suggesting that fumarolic degassing of sulfur-rich volatiles creating extremely acidic fluids might drive this system leading to intense argillic alteration, rather than a hydrothermal convection system.

Main objectives for our work during the M86/4 cruise were (i) completion of our dataset by sampling more pore fluids with a high hydrothermal fluid component, (ii) inclusion of sediment geochemistry for studying fluid-sediment interaction; (iii) determination of chemical gradients (temperature, redox) across the known mineralized areas; (iv) evaluation of p,T conditions within the studied submarine hydrothermal systems at Palinuro and Panarea, and related phenomena like phase separation. To achieve these goals we sampled pore fluids by means of rhizon samplers, and sediments obtained by gravity coring.

Analytical methods - pore fluids.
Before usage all rhizon soil moisture samplers had been thoroughly cleaned and pre-treated in baths of dilute subboiled HCL and subboiled HNO_3, and were then stored in ultrapure water. Pore fluid sampled with rhizons is 0.1 µm *in-situ* filtrated by principle through a micro-porous membrane (Seeberg-Elverfeldt et al., 2005). For each sampled sediment depth one pore fluid aliquot (2 ml) was stored in an acid-cleaned HDPE mini vial (2ml, Eppendorf) and acidified with 50 µl concentrated subb. HNO_3. These samples will be analysed for As, Sb, Bi;, Rb, Li, Cs; Sr, Ba; REEY; Fe, Mn, Co, Cu, Ag, Zn, Cd, Pb, Tl, Sn; Mo, W, U by ICP-MS. Another aliquot of 2 ml was transferred into untreated HDPE mini vials (2 ml, Eppendorf) as original sample without further treatment but kept refrigerated until analysis. This aliquot will be used for the analysis of Cl, Br, Si_T, B, Na, K, Rb, Li, Ca, Mg, Sr, Ba, Fe, Mn by ICP-OES, and Cl, SO_4 by IC. If enough pore fluid was available a third aliquot was transferred to 4 ml glass vials (Zinsser) for subsequent analysis of Hg by AFS. The pore fluid pH from at least 3 depths per sediment core

was analysed using the ion sensitive electrode InLab Micro-D in combination with a WTW 191 pH-Meter. The instrument was calibrated on a daily basis before each measurement using pH 4.0 and 7.0 certified reference solutions (Merck). A total of 240 pore fluid samples have been sampled for subsequent analysis (Appendix Table A1).

Analytical methods - sediments.
Sediment samples have been taken at same depths as pore fluid samples. Sampling was done by means of plastic spatula as core splitting was done with a nylon rope avoiding any contact of the sample with metal surfaces. Samples were stored in plastic zip bags and stored refrigerated until analysis in the home laboratories. Additional samples were taken for mineralogical analysis by XRD and polarized light microscopy. High resolution microanalysis of selected samples (e.g., orpiment-silica crusts) by electron probe (EPMA) and laser ablation-ICP-MS is planned. For the determination of bulk chemical composition all sediment samples will be homogenized, dried, milled and dissolved following a multi-step mixed acid protocol. Analyses will be performed with ICP atomic spectroscopic techniques ICP-OES; ICP-MS, AFS etc.. A total of 92 sediment samples have been stored for subsequent analysis (Appendix Table A2).

5.2.4 Sulfur Geochemistry at Palinuro and Panarea

(H. Strauss, M. Halama)

The Palinuro and Panarea volcanic complexes are characterized by massive sulfide and anhydrite occurrences that are covered by sediments of variable thickness. Previous research cruises (P340 in 2006, M73/2 in 2007, and P412 in 2011) recovered mineralized samples as well as hydrothermal fluids, sediment samples and sediment pore waters. Previous studies (e.g., Peters et al., 2011; Petersen et al., 2013) revealed substantial spatial (and presumably also temporal) variability in the sulfur geochemistry at these two locations. In general, vertical sections as well as profiles, e.g., across the Palinuro Volcanic Complex display a gradient from a hydrothermal end-member (e.g., the hydrothermal fluid) to the normal marine realm (reflected by the seawater and the normal marine surface sediments). These gradients are discernible in the concentration of dissolved constituents, both in the emanating hydrothermal fluids and the sediment pore waters. With respect to sulfur, we refer to highly variable concentrations of dissolved sulfide. But also the sediments and the massive mineralization reveal spatial variability in mineralogy and sulfur isotopic composition.

In order to further investigate the sulfur geochemistry at the Palinuro and Panarea volcanic complexes, sediment coring was performed using a gravity corer. From the recovered cores, sediment and pore fluid samples were obtained and subsampled for sulfur geochemistry. Sediment coring was supplemented with seawater column sampling using a CTD-Rosette equipped with 24 Niskin bottles with 10l volume each. From these, subsamples for sulfate sulfur and oxygen isotope measurements were collected.

Analytical methods - Pore waters
For the pore fluids, the concentration of dissolved sulfide was determined via spectral photometry. Analyses were done from 1ml aliquots using a zinc acetate gelatin solution, which precipitates the dissolved sulfide as colloidal zinc sulfide. Subsequently, the color agent, N,N-

dimethyl-1,4-phenylenediamine-dihydrochloride, and a catalyst, iron chloride solution, were added to form methylene blue (Cline, 1969). After 1 h, the solutions were measured photometrically at a wavelength of 670 nm using a Genesys 10 spectro-photometer. The detection limit was at 0.5 µmol/L. Potential oxidation of dissolved hydrogen sulfide during sampling cannot be ruled out, but should have been minimal. Still, concentration data reported are considered as minimum values.

Hydrogen sulfide dissolved in the pore fluids was precipitated as zinc sulfide with a 3% zinc-acetate solution. In the home laboratory, this will be measured for the four stable sulfur isotopes (^{32}S, ^{33}S, ^{34}S, ^{36}S).

From the same pore fluid samples, dissolved sulfate will be recovered as barium sulfate precipitate and also measured for its multiple sulfur and oxygen (δ18O) isotopic composition. Selected pore fluid samples were subsampled for measuring the carbon isotopic composition of dissolved inorganic carbon (δ13CDIC). 4ml aliquots were fixed with two drops of mercury chloride in order to prevent further microbial carbon turnover. Additional pore fluid subsamples were collected from selected gravity cores in order to evaluate the mixing between hydrothermal fluid and seawater through the analysis of oxygen isotopes.

Analytical Methods - Sediments

The sediment cores display a high degree of lithological variability. This includes unconsolidated oxic and anoxic sediments, some containing differently altered volcanoclastics, and layers composed of sulfide clasts as well as clayey sediments impregnated with euhedral pyrite cystals. Only for a few gravity cores, the oxic brown top sediment was recovered.

Sediment samples were collected usually at the same depth where pore water samples had been collected before. Original sedimentary material was obtained for determining the total sulfur, total carbon, and inorganic carbon concentrations in the home laboratory. To an additional subsample, 10ml of a 3% zinc acetate solution was added in order to stabilize the sulfide in these samples. These samples will subsequently been used for measuring the multiple sulfur isotope geochemistry of different sulfur species using a sequential wet chemical preparation procedur (modified after Rice et al., 1993).

Analytical Methods – Water column samples (CTD-Rosette)

Dissolved seawater sulfate was precipitated as barium sulfate for stable isotopic analyses of sulfur and oxygen. For this, aliquots of seawater were heated to near-boiling, acidified with HCl to a pH of ≤ 2 followed by the addition of 10% v/v of barium chloride solution. The sample was kept at 70°C for a few hours, cooled down and the barium sulfate was filtered off.

Preliminary Results

At the Palinuro Volcanic Complex, gravity coring was performed in order to map out the areal extent of a possible hydrothermal influence, following respective results from previous research cruises. Accordingly, clear differences exist in respect to the concentration of dissolved sulfide in the pore waters with a range between below detection limit (i.e. <0.5µmol/L) and 3487µmol/L. It is suggested that this results, at least in part, from the geographical position in respect to the known area of mineralization. Gravity core #270GC showed dissolved sulfide concentrations above 1000µmol/L throughout the entire length of the sediment core (except at 10cm with 573µmol/L). Elevated sediment temperatures were measured on deck (58°C at 300cm, 26°C at the top of the core), which would be consistent with a hydrothermal influence that could be (at least part of) the source of the dissolved sulfide. The sediment core #273GC exhibits a completely different picture showing essentially no dissolved sulfide in all pore water samples except for the lowest part of the core. Below 250cm, dissolved sulfide values between 68 and 626µmol/L were measured. At a depth of 300cm, a sediment temperature of 26.8°C was measured.

Gravity core #277GC displays a gradual increase in dissolved sulfide concentration with increasing depth. Values are <1000µmol/L down to a depth of 190cm. Thereafter, concentrations are as high as 3487µmol/L. A hydrothermal influence is suggested and a maximum sediment temperature of 39°C (at 300cm) would be consistent with this implication. A distinct depth variation is discernible in sediment core #285GC. While the first 130cm contain essentially no dissolved sulfide, the lower part of the core (i.e. lower than 130cm) is characterized by concentrations of dissolved sulfide between 600 and 1940µmol/L. Again, a correlation with sediment temperature is indicated with temperatures between 38.1°C at 300cm and 28.4°C at 200cm depth. Variable dissolved sulfide concentrations were measured for #287GC. Concentrations are <1000µmol/L in the top 190cm of the sediment core, followed by concentrations >1000µmol/L in the lower part of the sediment core. The elevated concentrations of dissolved sulfide could reflect a hydrothermal influence, consistent with elevated sediment temperatures between 25.2 and 40.0°C. Almost all pore water samples from #291GC are characterized by dissolved sulfide concentrations below detection limit. Only pore waters from the lower part of the sediment core yielded values around 1µmol/L. Sediment temperatures are also low between 12 and 19.9°C. Gravity core #304GC was fully oxidized. Sediment temperatures were between 13 and 15°C, and no hydrogen sulfide odor was discernible. Hence, pore waters were not measured for their dissolved sulfide concentration.

At the Panarea Volcanic Complex, two gravity cores were recovered (#294GC and #296GC). Sediment temperatures were 14.0 and 23.6°C. Although slightly elevated temperatures suggested a possible hydrothermal signal, almost all pore water samples yielded dissolved sulfide concentrations below detection limit. Only for the depth interval between 30 and 170cm in #294GC, concentrations ranged between 1.0 and 12.6µmol/L.

An exploratory gravity core was recovered from the Glabro Volcanic structure (#302GC). No pore water samples were collected for sulfur geochemistry from the yellowish to olive green sediment.

5.2.5 Arsenic speciation in hydrothermal fluids

(C. Breuer und P.-J. Sahr)

Arsenic is ubiquitously present in the environment with concentrations of around 0.62 µg L^{-1} in rivers (Gaillardet et al., 2003) and with a mean concentration of 1.7 µg L^{-1} in the global oceans (Neff, 2002). Contrasting to these, arsenic (As) concentrations in hydrothermal fluids are considerably higher due to water-rock interactions at elevated temperatures and additional input of magmatic volatiles. Thereby, the highest values were measured at island arc settings compared to lower values at mid-ocean ridges and back-arc basins due to different source rock composition and various other (local) factors. Maximum endmember values (Mg=0) measured for mid ocean ridges were around 80.5 µg L^{-1} at the Guaymas basin and 1390 µg L^{-1} at the PACMANUS site in the Manus back-arc basin. Hydrothermal systems at island arcs show values which are several magnitudes higher like at Milos where hydrothermal fluid endmember contain 5850 µg L^{-1} of As.

In aqueous systems, As can occur in different valency or oxidation states of +5, +3, 0 and -3, whereas the first two are the most important (Sharma & Sohn, 2009). In hydrothermal fluids, with low pH and reducing conditions, the trivalent arsenite should be the dominating species, which could be easily oxidized requiring good preservation. Samples for the total amount of As in the hydrothermal pore fluids were acidified with HCl to higher solubility and prevent precipitation with Fe and Mn and afterwards stored and transported cool at 4°C. Considering samples for speciation these were immediately cryofrozen and transported at -20°C until HPLC-ICP-MS measurements. Additional solid samples were taken from the cores to analyse these for their As concentration and top-sediments for As lipids.

5.3 Metagenomics

(C. Acquisti, D. Meier, H. Strauss)

Rationale

The environmental availability of nutrients is emerging as a force shaping evolutionary change (Elser et al., 2011). Growth and reproduction in most ecosystems are critically constrained by the availability of nitrogen (Elser et al., 2007), an element that is an essential component of nucleotides and amino acids. Focusing on well-established genetic model organisms, several lines of evidence suggest a pivotal role of environmental limitation of N in shaping proteome and genome composition between (Acquisti et al., 2009a, b; Bragg and Hyder, 2004) and within (Acquisti et al. in preparation) species. However, these advances have primarily relied on genetic model organisms, inferring their role in the trophic chain based on major eco-physiological traits of species. For example, few bacteria and plant model organisms have been used as representative of primary producers and contrasted to few animal and fungi model organisms, considered as consumers (Acquisti et al., 2009a, b). A thorough quantification of the strength of natural selection exerted by environmental N availability from the abiotic environment to the genetic architecture of organisms in natural ecosystems is still lacking. Recent advances in metagenomics and metatranscriptomics allow to further extend our understanding of the genetic basis of adaptation to environmental challenges in natural communities. The tremendous potential of this approach primarily relies on the possibility to identify pools of functional genes involved in the key biogeochemical reactions directly in natural ecosystems, inferring a picture of the microbial community composition and biological activity in the environment.

Aims and Hypotheses

Following the biogeochemical cycling of N along a depth gradient within the marine water column, our aim here is to evaluate the evolutionary consequences of environmental availability of N on the material costs of genetic change across trophic levels using the power of metatranscriptomics in an evolutionary context. Under conditions of severe N limitation, growth and reproduction of individuals with lower allocation of N in their genes should be favored by natural selection. Thus, species exposed to chronic N limitation are expected to exhibit a progressive evolutionary shift in the frequencies of nucleotides towards an enrichment of nucleotides that contain lower relative concentration of N (compared to carbon). The availability of nutrients varies substantially across the water column, with sea surface environments poor in nutrients and exposed to high light intensity and deep-sea environments at lower light intensity, limiting photosynthesis. Thus, the marine water column provides an ideal set of related ecosystems to study the effect of environmental nutrient limitation on the evolution of protein and transcript composition.

In this project we will identify bacterial community composition, and transcript sequences and relative abundance at different depths along the water column. Furthermore, we will directly estimate the availability of N across the water column by measuring dissolved inorganic and organic N. In this context, the analysis of the evolutionary dynamics of highly expressed transcripts and proteins in the different microbial communities adapted to different ocean depths (and to different nutrient limitations), will allow us to directly link the environmental availability of N to different adaptive strategies of genome evolution.

Sampling stations and depths

The water was sampled along the depth of the water column from surface to seafloor in seven different stations in the Palinuro Volcanic Complex (Fig. 5.13). Station locations were chosen in regions of deep waters, ranging from 1900m to 3300 m depth. Using a CTD rosette, we monitored water parameters along the water column, and based on the local dynamics of temperature variation, the sampling depths were selected. We found temperature variation to be consistent in the four sampling stations located in the south of the Palinuro Volcanic Complex; surface water samples were collected at 5 m depth, middle depth samples at 1300 m, and the deep water samples were taken at 50 meters above the sea floor.

The choice of 1300 m reflected a significant step in the parameters recorded along the water column, indicating the presence of different bodies of waters (e.g., above and below 1330 m) with low mixing potential. This is extremely important when the goal of the project is to identify specific patterns of genome composition of microbial communities exposed to different levels of light and nutrient availability over evolutionary time scales.

Table 2: CTD-Multirosette sampling station coordinates

Station ID	Date	Latitude	Longitude	Depth (m)
269CTD	02/10/12	39°24.05' N	14°40.45' E	2975
274CTD	02/11/12	39°23.00' N	14°46.00' E	2692
278CTD	02/12/12	39°39.00' N	14°46.00' E	1900
283CTD	02/13/12	39°39.00' N	14°40.05' E	1990
290CTD	02/14/12	39°13.00' N	14°49.00' E	3310
298CTD	02/15/12	38°49.00' N	14°50.50' E	2825
300CTD	02/16/12	38°56.00' N	15°06.00' E	2590

Sampling microbial communities via filtration

At each depth we collected 50 litres of water with the CTD rosette. 40 litres were used for a double filtration to separate microbial communities based on cell size (Fig. 5.14). A combined pre-filtration with filter with pore size 10 and 2.7 µm, followed by a filtration with pore size 0.7 and 0.2 µm was performed on each water sample. In the first step of filtration prokaryotic cells associated to unicellular eukaryotes were isolated, while subsequently, in the second step free-living prokaryotic organisms were isolated. In order to preserve RNA, filters were shock-frozen in liquid nitrogen immediately after filtration and stored at -80°C.

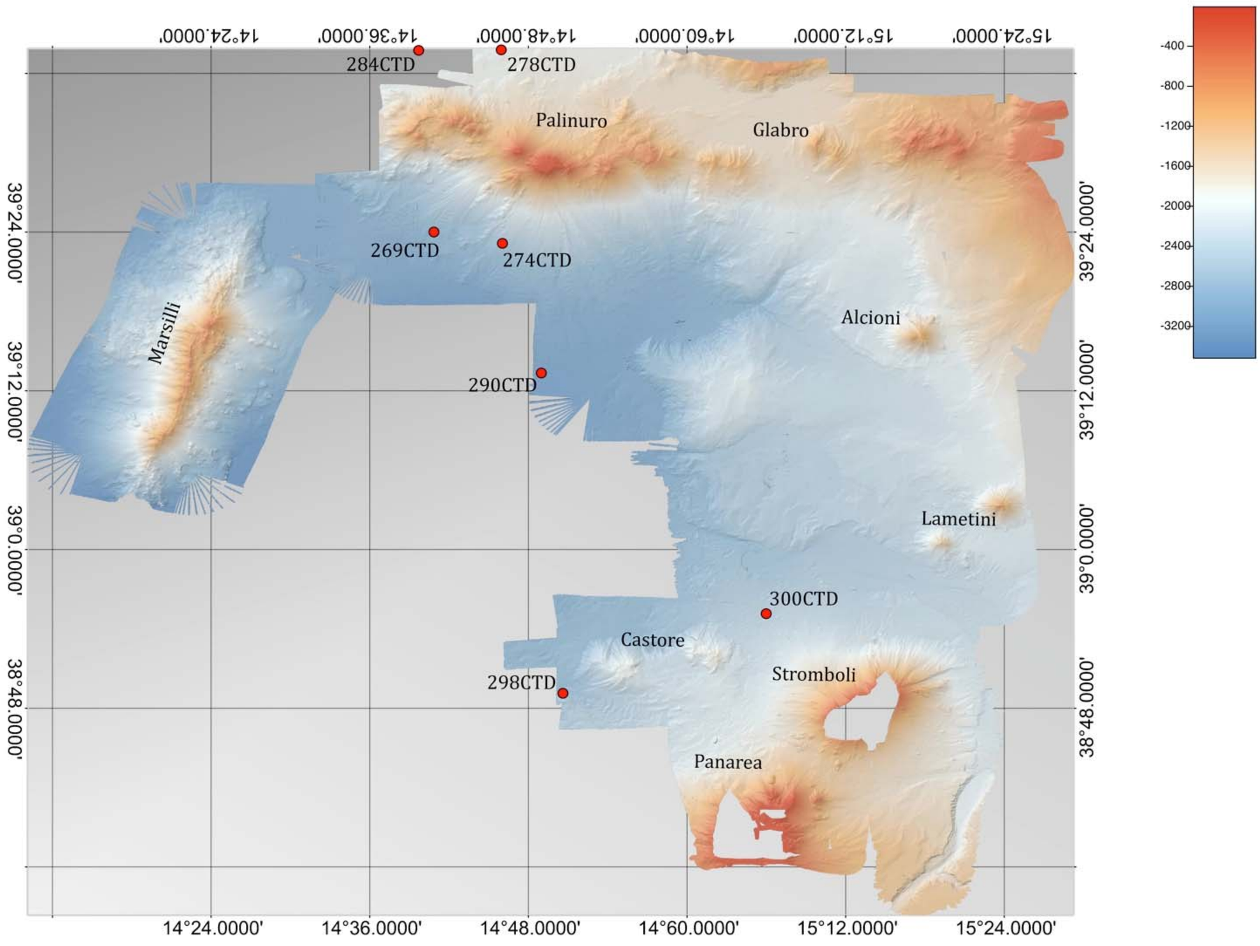

Fig. 5.13: Water sampling stations taken during cruise M86/4.

Sampling waters for availability of dissolved mineral and organic nitrogen

Along the depth profile, water samples were collected to quantify the availability and nitrogen (and oxygen) isotopic composition of selected nitrogen compounds. 200ml of water were frozen at -80°C, and nitrate/nitrite concentrations will be measured via spectral photometry at the home laboratory. Moreover, the stable nitrogen and oxygen isotopic compositions will be determined on the dissolved nitrate. For surface (5m depth), mid-water (1300m depth) and deep water (50m above the seafloor) samples, 4-9 litres of water were filtered through pre-combusted Whatman filters (0.47µm pore size) in order to collect particulate organic matter for nitrogen and organic carbon isotope measurements. Filters were frozen at -80°C. For selected profiles, subsamples were taken for the subsequent measurement of the C-isotopic composition of dissolved inorganic carbon.

Metatranscriptomics

At the home institutions, the total RNA will be extracted from each sample, and transcribed into cDNA by reverse transcription. The cDNA will be sequenced by Roche's 454 pyrosequencing, and analzyed.

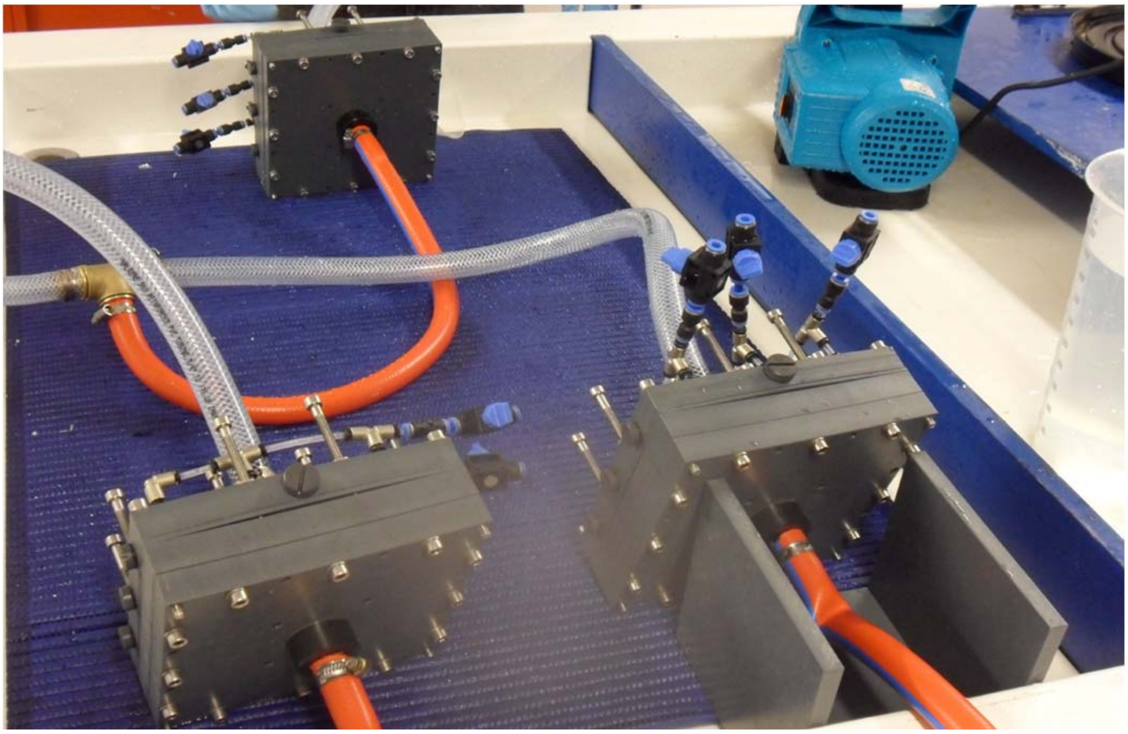

Fig. 5.14: Filtering apparatus for water column samples.

6 Ship´s Meteorological Station

On the 6th of february 2012 at night the vessel left the port of Dubrovnik. The sky was cloudy to overcast with a southeasterly wind of strength 5 Bft. The main working area was confined to the Aeolian island arc in the Tyrrhenian Sea to study geological issues. At first, the cruising area was influenced by a Russian high pressure ridge extending to the Balkans and a low over Sicily moving gradually to the Ionian Sea. The weather pattern favoured the development of the Bora in front of the Dalmatian coast. On the way to the working area FS METEOR passed the port of

Ploce to the north of Dubrovnik along the croatian coast. In open water (no shelter from land) the vessel experienced a sea from 1 to 2 m with a wind strength of 7 to 8 Bft from the Northeast to east.

On the morning of the 07th a "Bora" brought dry (about 35% humidity) winds of force 8 Bft, at times 9 Bft with gusts 10 Bft from the northeast. Along the coast the wind caused swirling sea spray. Due to the strong winds in the port, the crane work was stopped, which caused a longer stay until noon in the harbour. The cold air outbreak brought a few centimeters of snow to the port. The air temperature was about 1 to 2°C however due to the strong airflow the wind chill was much lower. In the evening FS METEOR continued its transit towards the Tyrrhenian Sea through the Strait of Messina. The low was almost stationary in the Ionian Sea. It gradually filled until the 09th. On the 8th FS METEOR still experienced easterly winds of force 7 to 8 Bft and a sea about 2.5 meters. On the 09th during the afternoon the protection of land in southern Italy or in the Straits of Messina favoured the wind to abate at times.

On the night to the 10th FS METEOR reached the working area. At the same time a low pressure system formed in the Tyrrhenian Sea. During the day of the 10th at the edge of the low a southwest wind with strength of 8 Bft was measured. Towards the evening the sea increased to 3 m. On the 11th the working area was in the center of the low.The wind decreased to an average of 3 to 4 Beaufort. However at times in showers the wind increased to 5 to 6 Bft. The sea/swell reached a height of 0.5 to 1m. Until the 16th FS METEOR stayed in the center of the low experiencing frequent showers with rain, graupel and at times thunderstorms. At night occasional lightning was observed. On the 15th a low was located near Corse. This caused a strong Mistral in the western Mediterranean to develop. In the working area close to the low the winds picked up to 6 to 7 Bft. The sea/swell rose to 2 to 2.5 m. On the 16th there was a strong pressure rise. An Atlantic ridge calmed the situation in the western Mediterranean. The wind shifted to the north with cold and dry air to follow. The visibility was excellent.

On the 17th the wind abated to 3 to 4 Bft with a sea/swell decreasing to 0.5 to 1m during the course of the day. On the transit to Palma de Mallorca low air pressure differences over the Mediterranean caused the wind to drop to 3 Beaufort with sea/swell of about 0.5 to 1 m, temporary under 0,5m and omnidirectional wind on 19th.

On the morning of the 20th the wind picked up to 4 to 5 Bft on while FS METEOR reached the final port of Palma de Mallorca.

7 *Station list M86/4* (K. Wegmann)

		START					END			
Station	**Gear Abbrev.**	**Date**	**Time**	**PositionLat**	**PositionLon**	**Depth [m]**	**Date**	**Time**	**PositionLat**	**PositionLon**
M864/267	SVP	09.02.12	19:46	38°56.98'N	15°19.03'E	2446	09.02.12	21:18	38°56.98'N	15°19.03'E
M864/268	MB / Multibeam	09.02.12	21:46	38°56.98'N	15°19.03'E	-	10.02.12	08:19	39°28.35'N	14°36.00'E
M864/269	CTD/RO	10.02.12	09:05	39°24.05'N	14°40.47'E	2988	10.02.12	11:18	39°24.00'N	14°40.51'E
M864/270	GC	10.02.12	12:42	39°32.40'N	14°42.39'E	633	10.02.12	13:42	39°32.40'N	14°42.39'E
M864/271	MB / Multibeam	10.02.12	15:16	39°27.94'N	14°36.00'E	-	11.02.12	05:33	39°35.32'N	15°26.76'E
M864/272	GC	11.02.12	09:03	39°32.40'N	14°42.37'E	630	11.02.12	09:48	39°32.40'N	14°42.37'E
M864/273	GC	11.02.12	09:57	39°32.39'N	14°42.37'E	629	11.02.12	10:37	39°32.39'N	14°42.37'E
M864/274	CTD	11.02.12	11:48	39°23.00'N	14°45.99'E	2701	11.02.12	13:39	39°23.00'N	14°46.00'E
M864/275	GC	11.02.12	14:55	39°32.20'N	14°41.97'E	724	11.02.12	15:38	39°32.19'N	14°41.94'E
M864/276	MB / Multibeam	11.02.12	17:31	39°31.68'N	15°07.53'E	-	12.02.12	06:35	39°33.42'N	15°24.05'E
M864/277	GC	12.02.12	09:30	39°32.40'N	14°42.42'E	638	12.02.12	10:09	39°32.40'N	14°42.41'E
M864/278	CTD	12.02.12	11:05	39°39.02'N	14°46.02'E	1901	12.02.12	12:46	39°39.00'N	14°46.01'E
M864/279	GC	12.02.12	13:44	39°31.40'N	14°43.86'E	888	12.02.12	14:32	39°31.39'N	14°43.84'E
M864/280	MB / Multibeam	12.02.12	14:54	39°32.07'N	14°44.30'E	-	13.02.12	06:06	39°14.37'N	15°19.83'E
M864/282	GC	13.02.12	08:18	39°30.61'N	14°56.29'E	802	13.02.12	09:05	39°30.59'N	14°56.29'E
M864/283	CTD	13.02.12	11:47	39°39.06'N	14°40.10'E	1991	13.02.12	13:24	39°39.00'N	14°40.01'E
M864/284	GC	13.02.12	14:21	39°31.42'N	14°42.42'E	1121	13.02.12	14:31	39°31.46'N	14°42.40'E
M864/285	GC	13.02.12	14:46	39°32.43'N	14°42.42'E	627	13.02.12	15:29	39°32.41'N	14°42.36'E
M864/286	MB / Multibeam	13.02.12	17:17	39°19.17'N	15°02.00'E	-	14.02.12	06:14	39°06.25'N	15°02.60'E
M864/287	GC	14.02.12	09:25	39°32.44'N	14°42.38'E	622	14.02.12	10:03	39°32.44'N	14°42.38'E
M864/288	CTD/RO	14.02.12	12:07	39°12.99'N	14°49.00'E	3304	14.02.12	12:12	39°12.99'N	14°49.00'E
M864/289	SVP	14.02.12	13:16	39°12.99'N	14°49.00'E	3304	14.02.12	15:38	39°13.00'N	14°49.00'E
M864/290	CTD/RO	14.02.12	15:56	39°13.00'N	14°49.00'E	3310	14.02.12	18:34	39°13.00'N	14°49.00'E
M864/291	GC	14.02.12	20:24	39°32.44'N	14°42.39'E	625	14.02.12	21:14	39°32.42'N	14°42.36'E
M864/292	MB / Multibeam	14.02.12	22:33	39°21.77'N	14°52.71'E	-	15.02.12	07:13	38°56.38'N	15°02.95'E
M864/293	MB / Multibeam	15.02.12	08:51	38°38.99'N	15°08.93'E	-	15.02.12	09:55	38°38.95'N	15°06.32'E
M864/294	GC	15.02.12	10:05	38°38.96'N	15°06.40'E	75	15.02.12	10:18	38°38.95'N	15°06.39'E
M864/295	MB / Multibeam	15.02.12	10:26	38°38.95'N	15°06.39'E	72	15.02.12	11:31	38°38.95'N	15°06.42'E
M864/296	GC	15.02.12	11:32	38°38.95'N	15°06.42'E	77	15.02.12	11:44	38°38.94'N	15°06.42'E
M864/297	MB / Multibeam	15.02.12	12:29	38°38.92'N	15°07.44'E	-	15.02.12	13:31	38°38.92'N	15°06.29'E
M864/298	CTD/RO	15.02.12	15:30	38°48.99'N	14°50.51'E	2824	15.02.12	18:26	38°49.00'N	14°50.51'E
M864/299	MB / Multibeam	15.02.12	18:33	38°49.05'N	14°50.70'E	-	16.02.12	13:04	38°55.88'N	15°05.84'E
M864/300	CTD/RO	16.02.12	13:13	38°55.99'N	15°05.99'E	2588	16.02.12	15:03	38°55.99'N	15°05.99'E
M864/301	MB / Multibeam	16.02.12	15:12	38°55.93'N	15°06.29'E	-	17.02.12	06:24	39°30.53'N	15°16.78'E
M864/302	GC	17.02.12	06:58	39°30.45'N	15°10.84'E	1112	17.02.12	07:58	39°30.41'N	15°10.81'E
M864/303	MB / Multibeam	17.02.12	08:40	39°35.89'N	15°10.80'E	-	17.02.12	11:35	39°36.00'N	14°44.31'E
M864/304	GC	17.02.12	13:44	39°32.39'N	14°42.36'E	629	17.02.12	14:20	39°32.39'N	14°42.36'E

8 Data and Sample Storage

Archive and working halfs from gravity coring are stored at GEOMAR and the scientist responsible for getting access to the samples is: Dr. S. Petersen (email: spetersen@geomar.de). Subsample for geochemical analyses went to Dr. D. Garbe-Schönberg (University Kiel) and those for isotopic measurements to Prof. H. Strauß (University Münster). Data generated will be stored in the GEOMAR data management system after publication but latest at the end of 2015.

The bathymetric data is also stored at GEOMAR (responsible: Dr. N. Augustin; email: naugustin@geomar.de) and was incorporated into PANGAEA in 2013. Bathymetric data and metadata to all stations was also made available to the appropiate Italian authorities and INGV.

Samples taken for microbiological investigations are stored at the Institute for Evolution and Biodiversity at the University of Münster in the working group of Prof. C. Acquisti. Metatranscriptomics data generated from these samples will be made publicly available through the CAMERA portal (https://portal.camera.calit2.net/gridsphere/gridsphere) at the end of 2015.

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Table A-1: On-board analytical results, and list of pore fluid samples

Station: **M86-4 270 GC** Date: 10/02/2012 Lat /Long: 39° 32.401' N 14°42.392' E(meteor) 39° 32.400' N 14°42.378' E

	GC depth cm	GC corr. depth cm	2 ml CAU Majors, Anions (Majors, Anions) ml	1 ml CAU Trace metals (Trace metals) ml	2 ml CAU Hg (Hg AFS) ml	0.5 ml WWU H_2S ml	10 ml WWU d34S ml	1 ml WWU d13C ml	3.5 ml UB As speciation ml	0.5 ml UB As ml	T °C	pH	Eh mV	Conductivity mS	H_2S µM	Comments
1	5		/	/		/	/	/							/	
2	15		/	/		/	/	/							/	
3	25		/	/		/	/	/							/	
4	35		2	2		1,5	9	/	3,5		26,1				573	
5	45		2	2		1,5	8,5	/	3,5						1230	
6	55		2	2		1,5	10,5	/	3,5			6.4△/6.5*		68,2	2820	O2 0.53 mg/L
7	65		2	2		1,5	9,5	/	3,5						1140	
8	75		2	2		1,5	10	/	3,5			6.4△/6.5*		68,9	3400	O2 5.15 mg/L
9	85		2	2		1,5	8	/	3,5						2310	
10	95		2	2		1,5	10	/	3,5		37,7	6.5△/6.4*		68,9	2240	
11	115		2	2		1,5	10,5	/	3,5						1670	
12	135		2	2		1,5	6	/	3,5						2690	
13	155		2	2		1,5	9,5	/	3,5						2760	
14	175		/	/		/	/	/	/						/	
15	195		/	/		/	/	/	/		48,1				/	
16	215		2	2		1,5	4	/	3,5						3110	
17	235		2	2		1,5	6	/	2,0						2540	
18	255		2	2		1,5	6	/	1,5						3170	
19	275		2	2		1,5	7	/	1,0						3120	
20	295		/	/		/	/	/	/		58,1				/	

* messured by Pau △ measured by Bettina

Station: **M86-4 273 GC** Date: 11/02/2012 Lat /Long: 39° 32.401' N 14°42.385' E (Posidonia)

	GC depth cm	GC corr. depth cm	2 ml CAU Majors, Anions (Majors, Anions) ml	1 ml CAU Trace metals (Trace metals) ml	2 ml CAU Hg (Hg AFS) ml	0.5 ml WWU H_2S ml	10 ml WWU d34S ml	1 ml WWU d13C ml	3.5 ml UB As speciation ml	0.5 ml UB As ml	T °C	pH	Eh mV	Conductivity mS	H_2S µM	Comments
1	10		2	2		1,5			2	1	13,6				<0.2	
2	30		2	2		1,5			2	1		7.1*		57,6	<0.2	
3	50		2	2	4	1,5			2	1					<0.2	
4	70		2	2		1,5			2	1					<0.2	
5	90		2	2		1,5			2	1	16,3	7.2*		54,9	<0.2	
6	110		2	2		1,5			2	1					<0.2	
7	130		2	2		1,5			2	1					<0.2	
8	150		2	2	4	1,5			2	1					<0.2	
9	170		2	2		1,5			2	1		7.0*		56,3	<0.2	
10	190		2	2		1,5			2	1	20,6				1,4	
11	210		2	2		1,5			2	1					0,2	
12	230		2	2		1,5			2	1					1,3	
13	250		2	2		1,5			2	1		6.4△			68,2	
14	270		2	2	3,5	1,5			2	1					626	
15	290		2	1		1,5			2	1	26,8				172	

* messured by Pau △ measured by Bettina

Table A-1: contd.

Station: **M86-4 277 GC** Date: 12/02/2012 Lat /Long: 39° 32.410' N 14°42.404' E(Posidonia)

			2 ml	*1 ml*	*2 ml*	*0.5 ml*	*10 ml*	*1 ml*	*3.5 ml*	*0.5 ml*						
			CAU	CAU	CAU	WWU	WWU	WWU	UB	UB						
	GC depth	**GC corr. depth**	**Majors, Anions**	**Trace metals**	**Hg**	**H_2S**	**d34S**	**d13C**	**As speciation**	**As**	**T**	**pH**	**Eh**	**Conductivity**	**H_2S**	**Comments**
			Majors, Anions	Trace metals	Hg AFS											
	cm	cm	ml	ml	ml	ml	ml	ml	ml	ml	°C		mV	mS	µM	
1	10		2	2		1,5	8		2		17,5				0,3	top sediment is missing
2	30		2	2		1	8		2	1,5		6.96*			b.d.l.	~630 m
3	50		2	2		1	8		2						1,5	
4	70		2	2	4	1	8		2	1,5					16,3	
5	90		2	2		1	8		2		25,2				125	
6	110		2	2		1	8		2						303	
7	130		/	1,5		1	/		2						1010	
8	150		2	2		1	8		2						573	
9	170		/	/		/	/		/						509	
10	190		2	2		1	8		2						577	
11	210		2	2		1	8		2		26,4				3060	
12	230		2	2	4	1	8		2	1,5		6.28△			3490	
13	250		/	1,5		1	/		/						1060	
14	270		2	2		1	8		2						3420	
15	290		2	2		1	8		2		39,0				1970	
16																
17																
18																
19																
20																

* measured by Che △ measured by Bettina

Station: **M86-4 279 GC** Date: 12/02/2012 Lat /Long: 39° 31.394' N 14°43.838' E (Posidonia)

			2 ml	*1 ml*	*2 ml*	*0.5 ml*	*10 ml*	*1 ml*	*3.5 ml*	*0.5 ml*						
			CAU	CAU	CAU	WWU	WWU	WWU	UB	UB						
	GC depth	**GC corr. depth**	**Majors, Anions**	**Trace metals**	**Hg**	**H_2S**	**d34S**	**d13C**	**As speciation**	**As**	**T**	**pH**	**Eh**	**Conductivity**	**H_2S**	**Comments**
			Majors, Anions	Trace metals	Hg AFS											
	cm	cm	ml	ml	ml	ml	ml	ml	ml	ml	°C		mV	mS	µM	
1																883 m water depth
2																
3																Kein Porenwasser
4																Keine Proben
5																
6																normal sediment
7																not sampled

Station: **M86-4 282 GC** Date: 13/02/2012 Lat /Long: 39° 30.598' N 14°56.303' E

			2 ml	*1 ml*	*2 ml*	*0.5 ml*	*10 ml*	*1 ml*	*3.5 ml*	*0.5 ml*						
			CAU	CAU	CAU	WWU	WWU	WWU	UB	UB						
	GC depth	**GC corr. depth**	**Majors, Anions**	**Trace metals**	**Hg**	**H_2S**	**d34S**	**d13C**	**As speciation**	**As**	**T**	**pH**	**Eh**	**Conductivity**	**H_2S**	**Comments**
			Majors, Anions	Trace metals	Hg AFS											
	cm	cm	ml	ml	ml	ml	ml	ml	ml	ml	°C		mV	mS	µM	
1																
2																exploration site
3																800 m water depth
4																
5																40cm recovery
6																
7																no samples!

Table A-1: contd.

Station: **M86-4 285 GC** Date: 13/02/2012 Lat /Long: 39° 32.411' N 14°42.385' E

			2 ml	1 ml	2 ml	0.5 ml	10 ml	1 ml	3.5 ml	0.5 ml						
			CAU	CAU	CAU	WWU	WWU	WWU	UB	UB						
	GC depth	**GC corr. depth**	**Majors, Anions**	**Trace metals**	**Hg**	**H_2S**	**d34S**	**d18O**	**As speciation**	**As**	**T**	**pH**	**Eh**	**Conductivity**	**H_2S**	**Comments**
			Majors, Anions	Trace metals	Hg AFS					TOT						
	cm	cm	ml	ml	ml	ml	ml	ml	ml	ml	°C		mV	mS	µM	
1	10		/	/							13,8				b.d.l	
2	30		2	2		0,5	4		2	1,5					b.d.l	629 m water depth
3	50		2	2	4	0,5	6	2	2						b.d.l	
4	70		2	2		0,5	8		2	1,5					b.d.l	2,85 m recovery
5	90		2	2		0,5	7	2	2		20,3				b.d.l	
6	110		2	2		0,5	8	2	2	1,5		7,0			b.d.l	
7	130		2	2		0,5	8	2	2	1,5					5,1	
8	150		2	2		0,5	3		2	1,5					864	
9	170		2	2		0,5	8	2	2	1,5					1861	
10	190		2	2		0,5	/	2	2	1,5	28,4				1941	
11	210		/	/		/	/		/						1550	
12	230		/	/		/	/		2						1562	
13	250		2	2		0,5	/	2	2	1,5					1251	
14	270		2	2		0,5	/		2			6,7			868	
15	290		/	/		/	/		/		38,1				610	

Station: **M86-4 287 GC** Date: 14/02/2012 Lat /Long: 39° 32.437' N 14°42.390' E

			2 ml	1 ml	2 ml	0.5 ml	10 ml	1 ml	3.5 ml	0.5 ml						
			CAU	CAU	CAU	WWU	WWU	WWU	UB	UB						
	GC depth	**GC corr. depth**	**Majors, Anions**	**Trace metals**	**Hg**	**H_2S**	**d34S**	**d13C**	**As speciation**	**As**	**T**	**pH**	**Eh**	**Conductivity**	**H_2S**	**Comments**
			Majors, Anions	Trace metals	Hg AFS											
	cm	cm	ml	ml	ml	ml	ml	ml	ml	ml	°C		mV	mS	µM	
1	10								2		25,2				3	3 m recovery
2	30		2	2					2						303	630 m water depth
3	50		2	2					2						577	
4	70		/	/					/						bdl	
5	90		/	/					2		30,4				170	
6	110		2	2					2						444	
7	130		2	2					2						654	
8	150		2	2					2						501	
9	170		1,5	1,5					2						137	
10	190		2	2					2		29,2				718	
11	210		2	2					2						1380	
12	230		2	2					2						1360	
13	250		2	1,5					2						1267	
14	270		2	2					2			6,58			1077	
15	290		1,5	1,5					/		40,6				480	

Table A-1: contd.

Station: **M86-4 291GC** Date: 14/02/2012 Lat /Long: 39° 32.410' N 14°42.371' E

			2 ml	1 ml	2 ml	0.5 ml	10 ml	1 ml	3.5 ml	0.5 ml						
			CAU	CAU	CAU	WWU	WWU	WWU	UB	UB						
	GC depth	**GC corr. depth**	**Majors, Anions**	**Trace metals**	**Hg**	**H_2S**	**d34S**	**d13C**	**As speciation**	**As**	**T**	**pH**	**Eh**	**Conductivity**	**H_2S**	**Comments**
			Majors, Anions	Trace metals	Hg AFS											
	cm	cm	ml	ml	ml	ml	ml	ml	ml	ml	°C		mV	mS	µM	
1	10										12,0					
2	30															
3	50															
4	70														b.d.l	
5	90								2						b.d.l	
6	110	40	2	2		8			2	1,5	13,2				b.d.l	
7	130	60	2	2		8			2	1,5		7,37			b.d.l	
8	150	80	2	2		8			2	1,5					b.d.l	
9	170	100	2	2		8			2	1,5		7,53			0,6	
10	190	120	2	2		7			2						0,9	
11	210	140	2	2		8			2	1,5	15,1	7,35			b.d.l	
12	230	160	2	2		8			2	1,5					1,3	
13	250	180	2	2		8			2	1,5					0,9	
14	270	200	2	2	4	8			2			6,86			1,0	
15	290	220	2	2		2			2		19,9				b.d.l	

Station: **M86-4 294 GC** Date: 15/02/2012 Lat /Long: 38° 38.955' N 15°06.395' E

			2 ml	1 ml	2 ml	0.5 ml	10 ml	1 ml	3.5 ml	0.5 ml						
			CAU	CAU	CAU	WWU	WWU	WWU	UB	UB						
	GC depth	**GC corr. depth**	**Majors, Anions**	**Trace metals**	**Hg**	**H_2S**	**d34S**	**d13C**	**As speciation**	**As**	**T**	**pH**	**Eh**	**Conductivity**	**H_2S**	**Comments**
			Majors, Anions	Trace metals	Hg AFS											
	cm	cm	ml	ml	ml	ml	ml	ml	ml	ml	°C		mV	mS	µM	
1	10		2	2							15,9				b.d.l	75 m water depth
2	30		1	1											12,6	recovery
3	50		/	/											/	
4	70		/	/											/	
5	90		2	2							16,7	6,22			1,7	core degassing
6	110		/	/											/	
7	130		/	/											/	
8	150		2	2											1,0	
9	170		2	2								6,14			11,3	
10	190		/	/							17,0				b.d.l	
11	210		/	/											b.d.l	
12	230		/	/											/	
13	250		2	2											b.d.l	
14	270		1	1											b.d.l	
15	300		/	/							19,6					

Table A-1: contd.

Station: **M86-4 296 GC** Date: 15/02/2012 Lat /Long: 15°06.422' E 38° 38.942' N

	GC depth	GC corr. depth	2 ml CAU **Majors, Anions** Majors, Anions	1 ml CAU **Trace metals** Trace metals	2 ml CAU **Hg** Hg AFS	0.5 ml WWU **H_2S**	10 ml WWU **d34S**	1 ml WWU **d13C**	3.5 ml UB **As speciation**	0.5 ml UB **As**	**T**	**pH**	**Eh**	**Conductivity**	**H_2S**	**Comments**
	cm	cm	ml	ml	ml	ml	ml	ml	ml	ml	°C		mV	mS	µM	
1	10		2	2											b.d.l	76.4 m water depth
2	30		2	2	4							5,48			b.d.l	
3	50		1	1,5											b.d.l	
4	70															
5	90		2	2								5,72			b.d.l	
6	110		2	2											b.d.l	
7	130		1,5	1,5											b.d.l	
8	150															
9	170		2	2								5,77			b.d.l	
10	190															
11	210															
12	230															
13	250		2	2	4										b.d.l	
14	270		2	2								5,99			b.d.l	
15	290		1	1												

Station: **M86-4 302 GC** Date: 17/02/2012 Lat /Long: 15°10.801' E 39° 30.399' N

	GC depth	GC corr. depth	2 ml CAU **Majors, Anions** Majors, Anions	1 ml CAU **Trace metals** Trace metals	2 ml CAU **Hg** Hg AFS	0.5 ml WWU **H_2S**	10 ml WWU **d34S**	1 ml WWU **d13C**	3.5 ml UB **As speciation**	0.5 ml UB **As**	**T**	**pH**	**Eh**	**Conductivity**	**H_2S**	**Comments**
	cm	cm	ml	ml	ml	ml	ml	ml	ml	ml	°C		mV	mS	µM	
1	10		2	2	3						12,9					
2	30		2	2								7,17				Glaubra split volcano
3	50		2	2												1105 m water depth
4	70		2	2												3 m recovery
5	90		2	2							13,0	7,19				
6	130		2	2	4											
7	170		2	2								7,09				
8	210		2	2							13,0					
9	250		2	2												
10	280		2	2							13,4	7,16				

Table A-1: contd.

Station: **M86-4 304 GC** Date: 17/02/2012 Lat /Long: 14°42.370' E 39° 32.379' N

			2 ml	1 ml	2 ml	0.5 ml	10 ml	1 ml	3.5 ml	0.5 ml						
			CAU	CAU	CAU	WWU	WWU	WWU	UB	UB						
	GC depth	**GC corr. depth**	**Majors, Anions**	**Trace metals**	**Hg**	**H_2S**	**d34S**	**d13C**	**As speciation**	**As**	**T**	**pH**	**Eh**	**Conductivity**	**H_2S**	**Comments**
			Majors, Anions	Trace metals	Hg AFS											
	cm	cm	ml	ml	ml	ml	ml	ml	ml	ml	°C		mV	mS	µM	
1	10		/	/							13,2					
2	30		/	/												628 m water depth
3	50		/	/												recovery
4	70		/	/												
5	90		2	2	1						13,2	7,41			n.d	
6	110		2	2								6,90			n.d	
7	130		2	2								7,02			n.d	
8	150		2	2								6,69			n.d	
9	170		2	2	4							6,37			n.d	
10	190		2	2							14,7	6,38			n.d	
11	210		2	2								6,24			n.d	
12	230		2	2								6,20			n.d	
13	250		2	2								6,41			n.d	
14	270		2	2	4							6,38			n.d	
15	290		/	/							15,4					

Table A-2: List of sediment samples for bulk geochemical and mineralogical phase analysis

BULK	***MINERAL.***
Station	**270 GC**
27 cm	
35 cm	35 cm
45 cm	45 cm
55 cm	55 cm
67 cm	67 cm
79 cm	79 cm
86 cm	86 cm
94 cm	94 cm
115 cm	115 cm
135 cm	
155 cm	166 cm
	214 cm
Station	**273 GC**
15 cm	
80 cm	
170 cm	140 cm
250 cm	235 cm
Station	**277 GC**
10 cm	
40 cm	40 cm
90 cm	
103-105 cm	110 cm
150-152 cm	161-163 cm
225 cm	
250-252 cm	
Station	**285 GC**
1 cm	
56 cm	
145 cm	145 cm
146 cm	
	168 cm
242 cm	
262 cm	
269 cm	
272 cm	272 cm

BULK	***MINERAL.***
Station	**287GC**
40 cm	
121 cm	105 cm
141 cm	140 cm
156 cm	
170 cm	165 cm
174 cm	
Station	**291GC**
42-44 cm	core catcher
54-56 cm	30 cm (chimney
64-66 cm	
84-86 cm	80 cm
114 cm	
148-152 cm	150 cm
188-192 cm	
228-232 cm	
Station	**294GC**
30 cm	
150 cm	
270 cm	
Station	**296GC**
10 cm	
50 cm	50 cm
110 cm	
170 cm	170 cm
240 cm	240 cm
270 cm	
Station	**302GC**
10 cm	
130 cm	
280 cm	
Station	**304GC**
10 cm	
30 cm	
78 cm	
105 cm	
125 cm	
230 cm	
250 cm	
280 cm	

R/V Meteor M86/4	**Station: 270GC**
Location: Palinuro	Water depth: 633 m
Latitude: 39°32.400’ N	Recovery: 242 cm
Longitude: 14°42.378’ W	Date: 10.02.2012, 12:42 UTC

Depth (cmbsf)	Lithology
	0-24 cm: Core empty, sediment stuck in the core catcher 24-38 cm: T=26°C, pale yellowish green (10GY 7/2) to medium; dark grey (N4) 38-47 cm: greyish black (N2) with yellow spots (1 cm ø); 1-5 cm irregular sulfide crusts 47-60 cm: green-grey (5G 6/1), more sandy, yellow spots 60-70 cm: black (N1), more dry, w. yellow S°-layer (70-73 cm) 73-78 cm: dusty yellow green (5GY 5/2) 78-87 cm: light olive grey (5Y 5/2) 87-89 cm: clusty green layers (5G 3/2) 89-100 cm: medium light grey (N6); 89-95 cm: yellow spots 100 cm: T=37.7°C

#270GC (cont.)

100-120 cm: medium light grey (N6)

120-200 cm: greenish grey clay (5G 6/1); 164-168 cm: S°-aggregats;

170-180 cm: no core;

192-200 cm: no core

#270GC (cont.)

200-206 cm: no core

206-290 cm: T=48°C; greenish grey clay (5G 6/1) with irregularly distributed greyish-green altered pumice clusts

290 cm; End of core; T=58°C

R/V Meteor M86/4	**Station: 272GC**
Location: Palinuro	Water depth: 630 m
Latitude: 39°32.40' N	Recovery: no recovery
Longitude: 14°42.37' W	Date: 11.02.2012, 09:02 UTC
Depth (cmbsf)	Lithology
	No core recovery

R/V Meteor M86/4	**Station: 273GC**
Location: Palinuro	Water depth: 628 m
Latitude: 39°32.401' N	Recovery: 300 cm
Longitude: 14°42.385' W	Date: 11.02.2012, 10:00 UTC
Depth (cmbsf)	Lithology
	0 cm: T=13.6°C 0-20 cm: sediment is very oxidized, moderate brown (5YR 4/4) 20-70 cm: greyish green (10GY 5/2) with light brown spots (5YR 5/6) 70-100 cm: increasing of dark lance of ash lapilly, altered ash lapilly reoxidized

#273GC (cont.)

100-130 cm: T=16.3°C FeOOH-channel dusky yellow (5Y 6/4) rim of channel moderate brown (5Y 3/4);

110 cm: border, sediment is getting darker, dark grey (N3), sulfide aggregates, pore water rich, green spots getting less to the bottom;

150 cm: white barite spots;

155-165 cm: aquifer, black sulfide aggregates are pore water rich;

165-195 cm: only a few green spots

200 cm: T=20.6°C;

#273GC (cont.)

200-260 cm: matrix dark grey (N3), some green spots, black sulfide aggregates;

240 cm: black sulfide aggregates with white silica;

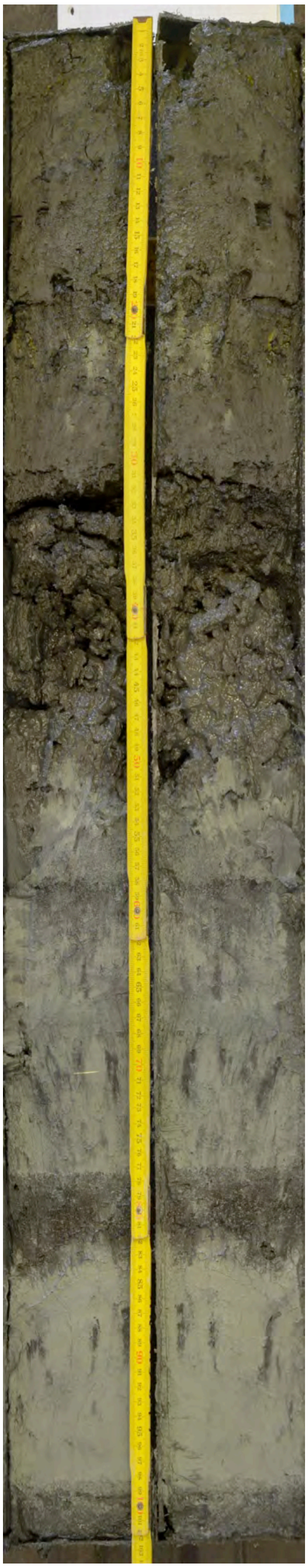
260-300 cm: sediment is getting greener, light pale olive green (10Y 6/2), white specks;

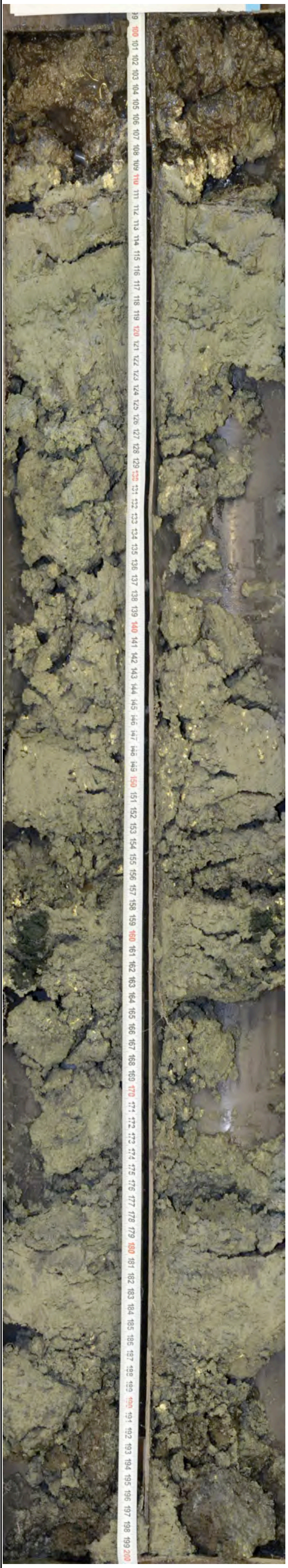
280 cm: sulfide layer;

300 cm; End of core; T=26.8°C

R/V Meteor M86/4	**Station: 275GC**
Location: Palinuro Latitude: 39°32.201’ N Longitude: 14°41.949’ W	Water depth: 725 m Recovery: 40 cm Date: 11.02.2012, 14:54UTC
Depth (cmbsf)	Lithology
	0-40 cm: dark yellowish orange (10YR 6/6), clay, homogenious sediment 40 cm; End of core

R/V Meteor M86/4	**Station: 277GC**
Location: Palinuro	Water depth: 638 m
Latitude: 39°32.410' N	Recovery: 300 cm
Longitude: 14°42.404' W	Date: 12.02.2012, 09:29 UTC

Depth (cmbsf)	Lithology
	0-21 cm: T=17.5°C matrix dark grey (N3), first five centimeters light olive brown spots (5Y 5/6), clay 21-24 cm: greyish green spots (5G 5/2) 24-50 cm: black (N1), pieces of sulfide crust in situ 50-80 cm: matrix greyish green (5G 5/2) with medium dark grey (N4) spots, 57 cm: black vein (silt) 80-100 cm: dark grey (N3) with black spots, matrix greyish green (5G 5/2), only a few black spots



#277GC (cont.)

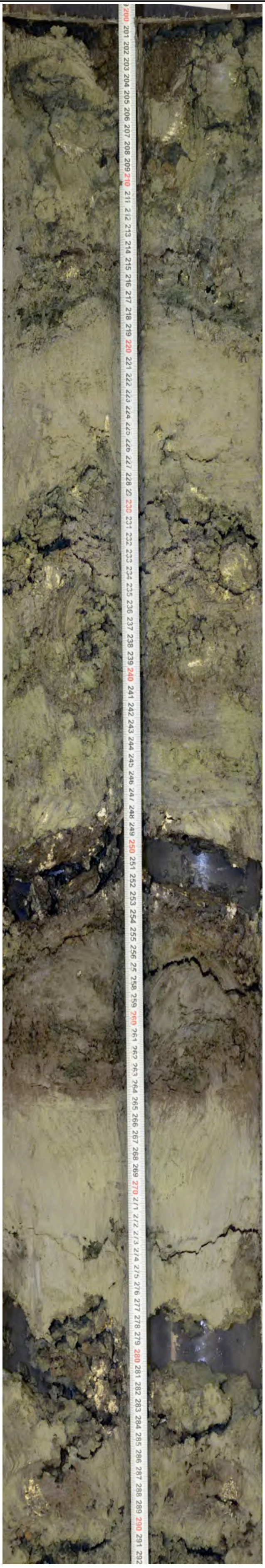
100-110 cm: T=25.2°C dark grey matrix (N3), black sulfide crusts, high water saturation

110-115 cm: yellow sulfur crusts

115-190 cm: greyish green matrix (10GY 5/2), clay with white sulfur spots; 157-163 cm: dusky yellowish green spot (10GY 3/2)

190-200 cm: greenish black (5G 2/1)

#277GC (cont.)



200 cm: T=26.4°C

200-250 cm: clay, greyish green (5G 5/2); 217 cm: dusky green (5G 3/2) vein

250-260 cm: medium dark grey (N4), clay, hydrothermal crusts (white), greyish black (5GY 2/1)

260-265 cm: brownish black (5YR 2/1), clay

265-300 cm: greyish green (5G 5/2) with dark grey spots (N3);

275 cm: dusky green spot (5G 3/2); 280 cm: white hydrothermal crusts;

300 End of core; T=39°C

R/V Meteor M86/4	**Station: 279GC**
Location: Palinuro	Water depth: 883 m
Latitude: 39°31.394’ N	Recovery: 275 cm
Longitude: 14°43.836’ W	Date: 12.02.2012, 13:42 UTC

Depth (cmbsf)	Lithology
	0-85 cm: moderate yellowish brown (10YR 5/4), clay; 20 cm: medium dark grey spots (N5); 40-45 cm: shellfragments, 45 cm: dark yellowish brown shadows (10YR 4/2); 60 cm: pale olive spot (10Y 6/2);

#279GC (cont.)

85 cm: coral, one mussel
85-275 cm: pale olive (10Y 6/2), clay;

118-125 cm: shellfragments;

150-154 cm: coarse sediment, ashlayer, greyish olive (10Y 4/2);

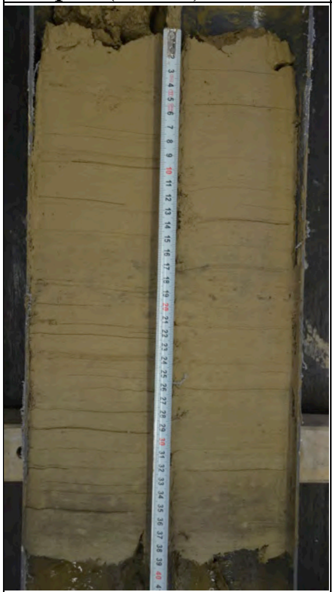
#279GC (cont.)

180 cm: shell fragments;

194-201 cm: shell fragments;

212-217 cm: shell fragments;

275 cm; End of core

R/V Meteor M86/4	**Station: 282GC**
Location: Palinuro	Water depth: 802 m
Latitude: 39°30.598' N	Recovery: 40 cm
Longitude: 14°56.303' W	Date: 13.02.2012, 08:20 UTC
Depth (cmbsf)	Lithology
	0-50 cm: dark yellowish orange matrix (10YR 6/6); 10-15 cm: black spots; 30-40 cm: bigger dark spots, clay 40 cm; End of core

R/V Meteor M86/4	**Station: 284GC**
Location: Palinuro Latitude: 39°31.40’ N Longitude: 14°42.39’ W	Water depth: 1166 m Recovery: no recovery Date: 13.02.2012, 14:21 UTC
Depth (cmbsf)	Lithology
	Station cancelled because of wrong positioning.

R/V Meteor M86/4	**Station: 285GC**
Location: Palinuro Latitude: 39°32.411’ N Longitude: 14°42.385’ W	Water depth: 629 m Recovery: 285 cm Date: 13.02.2012, 14:45 UTC
Depth (cmbsf)	Lithology
	0cm T=13.8°C 2-5 cm: dark yellowish orange layer (10YR 6/6); 5-120 cm: matrix dark greenish grey (5G 4/1), clay; with some dusky yellowish spots (5Y 6/4); 39-41 cm: dark yellowish orange spots (10YR 6/6); 95-120 cm: dark grey spots (N3), dusky yellow spots, two white spots, clay

#285GC (cont.)

125-167 cm: medium dark grey matrix (N4);

125-155 cm: black lense, clay

167-170 cm: white silica + sulfur layer, hard

170-175 cm: black layer with white sulfur spots, clay

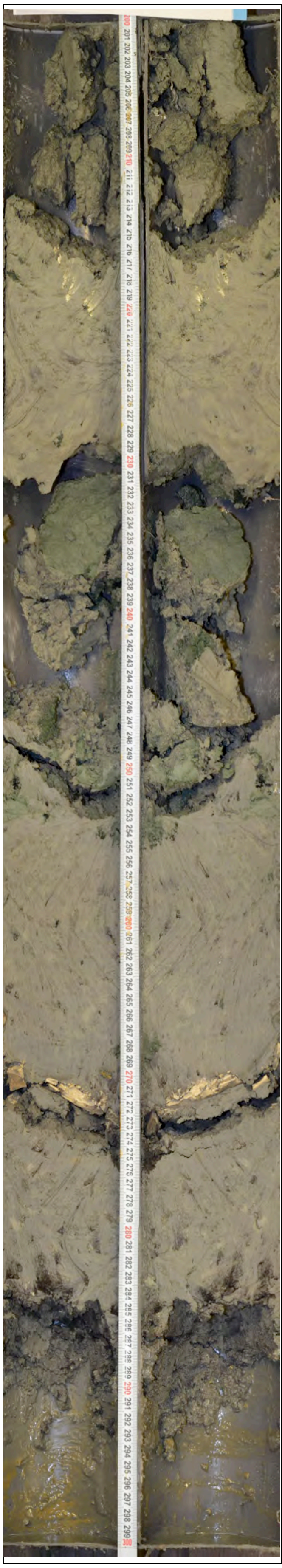
1
75-230 cm: dark greenish grey (5G 4/1);

187-230 cm: white sulfur spots; 180-190: black lens with white sulfur spots

190-230 cm: little black spots, clay

200 cm: T=28,4°C;

#285GC (cont.)



230-250 cm: altered pumice, dark yellowish green

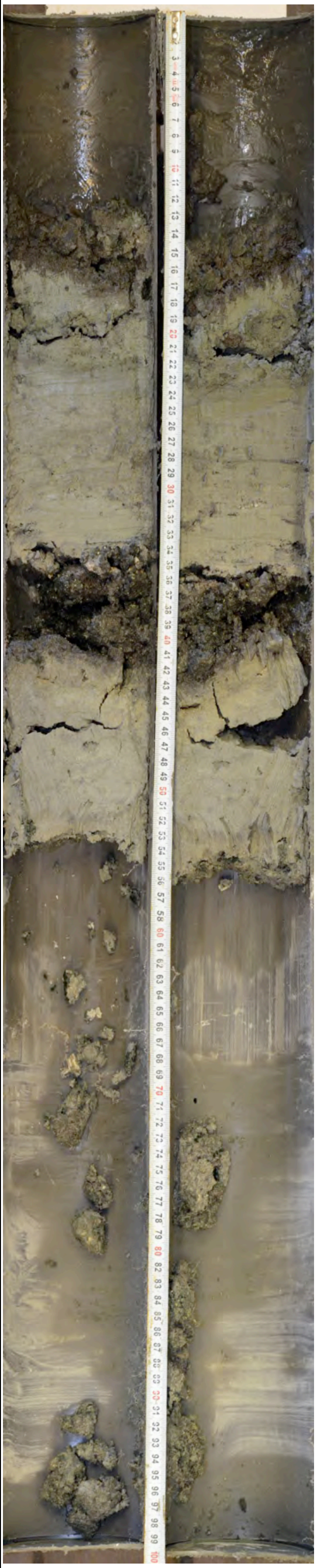
250-270 cm: matrix with little black spots, clay

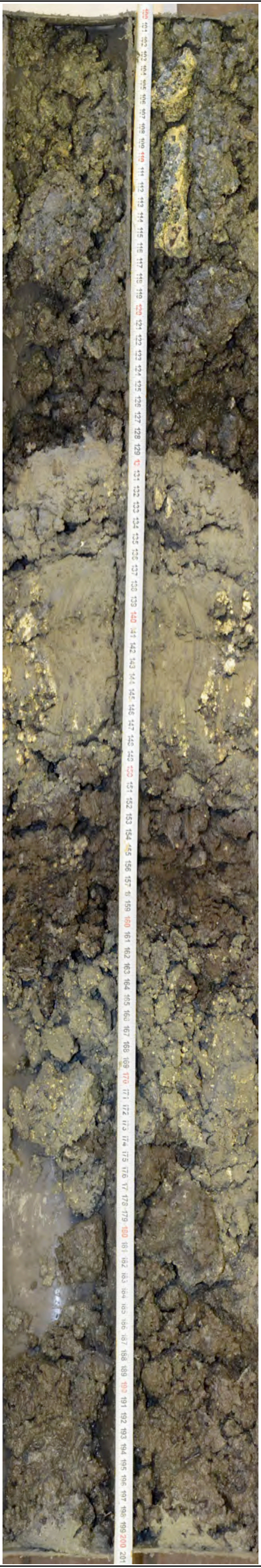
270-272 cm: white sulfur/ silica layer

272-285 cm: T=38.1°C , matrix with little black spots, clay

285 cm; End of core

R/V Meteor M86/4	**Station: 287GC**
Location: Palinuro	Water depth: 623 m
Latitude: 39°32.437’ N	Recovery: 242 cm
Longitude: 14°42.390’ W	Date: 14.02.2012, 09:28 UTC

Depth (cmbsf)	Lithology
	0-15 cm: no core 15-20 cm: T=25.2°C, dark grey (N3), water rich sediment, sulfide crusts 20-23 cm: dark greenish grey (5GY 4/1), vulcanoclastics 24 cm: dusky green (5G 3/2) 24-26 cm: light olive (10Y 5/4), clay 26-36 cm: greyish green (5G 5/2), clay; 31 cm: white silica spots, little black spot 36-44 cm: dark grey (N3), with white sulfur and silica spots, fine black spots, volcanoclastics 44-57 cm: dark greenish grey (5GY 4/1), clay 57-100 cm: no core



#287GC (cont.)

100-120 cm: T=30.4°C dusky green (10G 4/2) with white and yellow spots of sulfur aggregates and alterated sulfur (alterated volcanoclastics), volcanoclastics, silica

120-130 cm: black (N1), sulfide, clay, silt

130-153 cm: greyish green matrix (5G 5/2) + yellow sulfur grains, a few silica spots

153-165 cm: black, sulfur crusts

165-178 cm: greyish green matrix (5G 5/2), little yellow sulfur globules

178-200 cm: black sulfur crusts (N1)

#287GC (cont.)

200-210 cm: greyish green

210-212 cm: black layer (N1) with silica fragments
212-229 cm: yellow sulfur spots

229-233 cm: dark grey matrix (N3), yellow sulfur fragments

233-257 cm: greyish blue green (5BG 5/2), coarse black spots (N1)

257-270 cm: same sediment, but layer with more coarse spots, alterated volcanoclastic, dusky blue green (5BG 3/2), black (N1), sulfide

270-281 cm: greyish blue green (5BG 5/2), clay

281-300 cm: alterated volcanoclastics; 300 cm: T=40°C

300 cm; End of core

R/V Meteor M86/4	**Station: 291GC**
Location: Palinuro	Water depth: 625 m
Latitude: 39°32.410' N	Recovery: 257 cm
Longitude: 14°42.371' W	Date: 14.02.2012, 20:25 UTC
Depth (cmbsf)	Lithology
	0-33 cm: medium grey (N5), sulfide crusts, hydrothermal chimney pieces?, 12°C, <1 mm to 32 mm 33-40 cm: light brown matrix (5YR 5/6) with medium dark grey spots

#291GC (cont.)

40-47 cm: light brown (5YR 5/6), T=13.2°C, clay

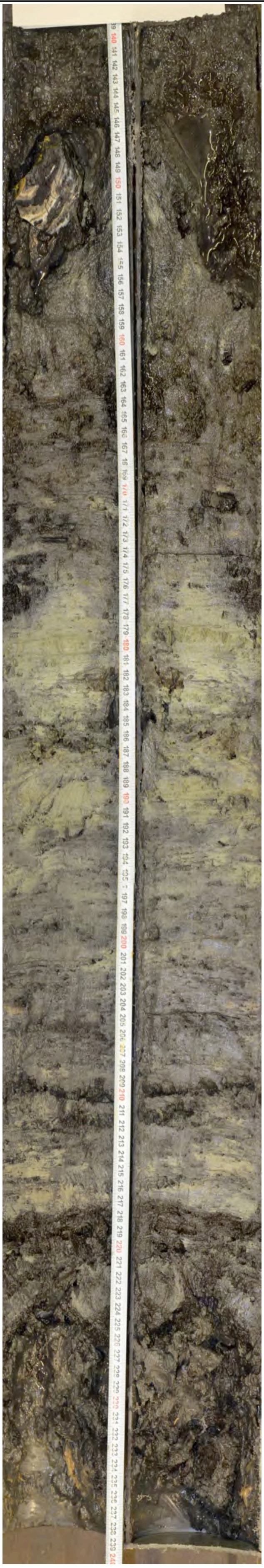
47-60 cm: dark yellowish orange (10YR 6/6), clay

60-70 cm: pale olive (10Y 6/2), clay

70-105 cm: medium blue grey matrix (5B 5/1) with greenish grey (5G 6/1) veins, black sulfide crusts

105-128 cm: dark grey matrix, clay, sulfide crusts

128-140 cm: medium dark grey (N4) matrix with greenish grey spots (5GY 6/1)



#291GC (cont.)

140-160 cm: T=15.1°C water saturated, dark grey matrix (N3), sulfide and silica crusts

160-180 cm: black sulfide crusts in matrix

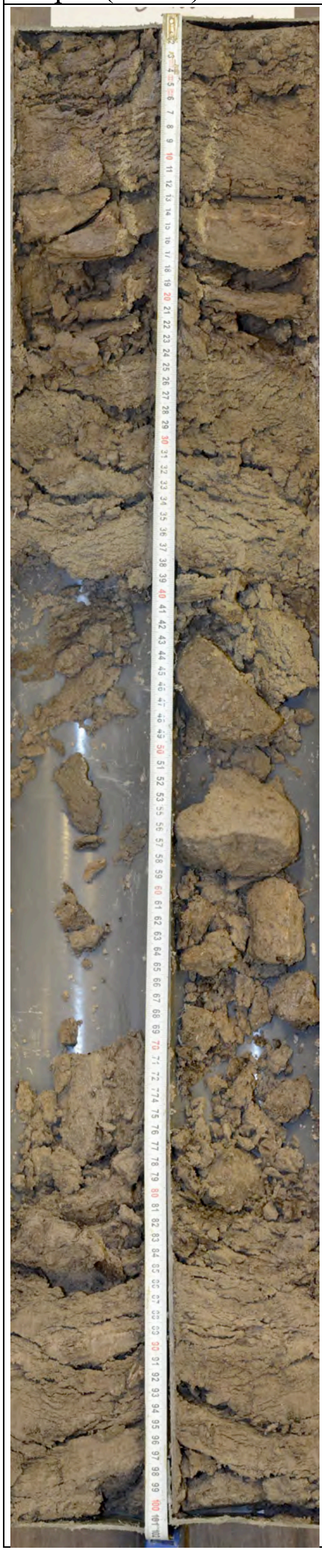
180-218 cm: medium bluish grey matrix (5B 5/1)

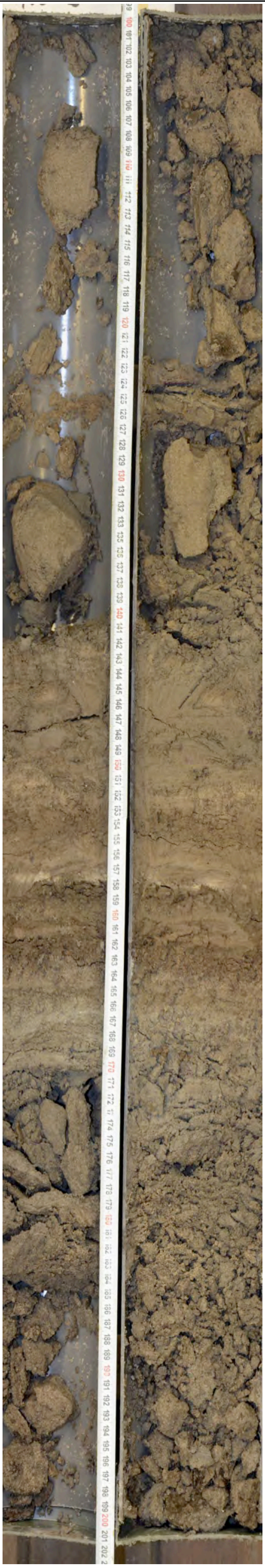
218-235 cm: big spots, greenish grey (5GY 6/1), black vein, dusky blue green vein (5BG 3/2)

235-237 cm: black matrix, clay, sulfide crusts; water saturated, T=19.9°C

237 cm; End of core

R/V Meteor M86/4	**Station: 294GC**
Location: Panarea	Water depth: 75 m
Latitude: 38°38.956’ N	Recovery: 220 cm
Longitude: 15°06.395’ W	Date: 15.02.2012, 10:03 UTC

Depth (cmbsf)	Lithology
	0-20 cm: dark yellowish brown (10YR 4/2), silty material, channel-looks like fluid/ gas – escape structure, decoloured 20-40 cm: pale, yellowish brown (10YR6/2), silty – fine sandy 40-80 cm: core empty 80-100 cm: dark yellowish brown (10YR 4/2), clay material contains what looks like plant detritus



#294GC (cont.)

100-140 cm: core empty

140-163 cm: interlayers of differently coloured material (dusky yellowish brown (10YR 2/2) – pale yellowish brown (10YR 6/2), clayey to silty

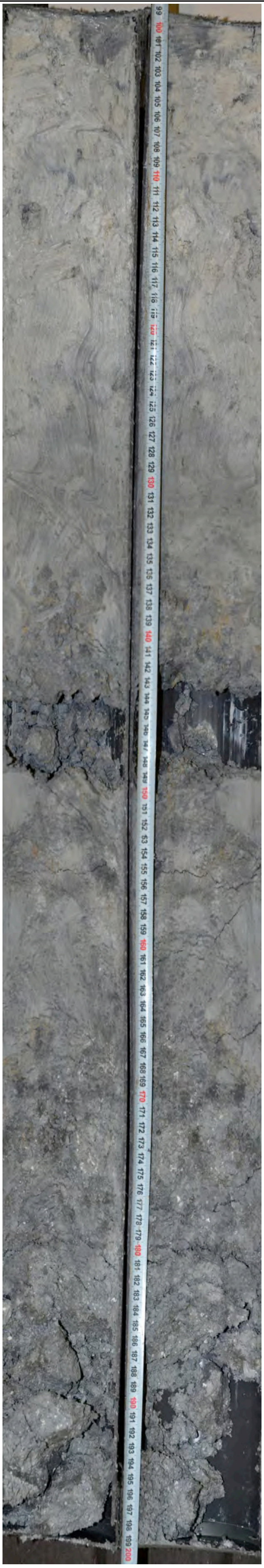
163-255 cm: dark yellowish brown (10YR 4/2), silty material to fine sandy

#294GC (cont.)

255-300 cm: dusky yellowish brown (10YR 2/2), clayey material, dry

300 cm; End of core

R/V Meteor M86/4	**Station: 296GC**
Location: Panarea	Water depth: 76 m
Latitude: 38°38.942’ N	Recovery: 240 cm
Longitude: 15°06.422’ W	Date: 15.02.2012, 11:32 UTC
Depth (cmbsf)	Lithology
	0-18 cm: T=14.2°C, bluish white (5B 9/1) to light bluish grey (5B 7/11), clay 18-28 cm: light olive grey (5Y 3/2), sandy material, oxidized at the top, shell fragments 28-98 cm: bluish white (5B 9/1) to light bluish grey (5B 7/11), clay, irregularly distributed sulfide crystals 98-105 cm: T=17.4°C, silt, clay fragments



#296GC (cont.)

105-145 cm: light bluish grey (5B 7/11) to light grey (N7), clay further down

145-150 cm: empty core

150-200 cm: T=18.0°C, light grey (N7) clay, coaser silty clay, white spots (N9), sediment, individual sulfide crystals (euhedral)

195-200 cm: empty core

#296GC (cont.)

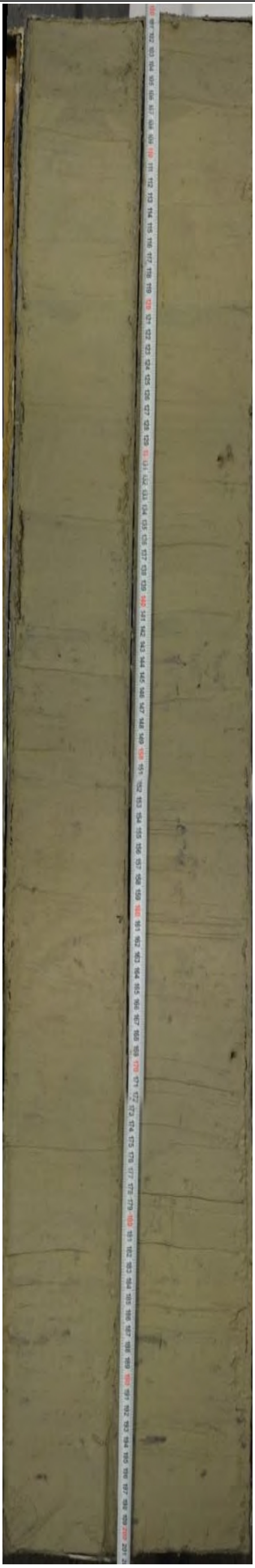
200-240 cm: empty core

240-290 cm: coase silty material, grey white spots, abundant individual euhedral sulfide crystals

290 cm: T=23.6°C; End of core

R/V Meteor M86/4	**Station: 302GC**
Location: Glabro	Water depth: 1112 m
Latitude: 39°30.399’ N	Recovery: 290 cm
Longitude: 15°10.801’ W	Date: 17.02.2012, 06:54 UTC
Depth (cmbsf)	Lithology
	0-45 cm: T=12.9°C dark yellowh orange (10YR6/6), oxidized horizon 45-285 cm: light olive grey (5Y5/2), 100 cm: T=13.0°C

#302GC (cont.)



120 cm: olive grey ash layer,

140 cm: green ash layer,
140-290 cm: black dots,

200 cm: T=13.0°C

#302GC (cont.)

290 cm; End of core; T=13.4°C

R/V Meteor M86/4	**Station: 304GC**
Location: Palinuro	Water depth: 628 m
Latitude: 39°32.379’ N	Recovery: 225 cm
Longitude: 14°42.370’ W	Date: 17.02.2012, 13:44 UTC
Depth (cmbsf)	Lithology
	0-20 cm: T=13.2°C, moderate yellowish brown (10YR 5/4), clay to silt 20-35 cm: greyish brown (5YR 3/2), clay to silt

#304GC (cont.)

35-45 cm: dark yellowish brown (10YR 4/2), oxidized sulfide, silica crusts, FeOOH

45-75 cm: light olive grey (5Y 5/2), clay

75-85 cm: light olive grey (10YR 4/2), oxidized sulfide crusts, FeOOH

85-100 cm: light olive grey (5Y 5/2), clay

100-125 cm: T=13.2°C, Dark yellowish brown (10YR 4/2), oxidized sulfide crusts with greenish sand (10GY 5/2), FeOOH

#304GC (cont.)

125-135 cm: black sulfide (?), oxidized, FeOOH

135-140 cm: dto. Brownish black (5YR 2/1), FeOOH

145-160 cm: dusky brown with grayish orange layer (10YR 7/4), oxidized sulfide (?), FeOOH, sand

160-180 cm: grayish yellow (5Y 8/4), grayish orange (10YR 7/4), laminated clay

180-185 cm: light olive grey (5Y 3/2), clay

185-200 cm: dark yellowish orange (10YR 6/6) with oxidzed sulfide crusts, FeOOH

200-210 cm: T=14.7°C, moderate yellowish brown (10YR 5/4), MnFeOOH clusts in clay matrix

210-225 cm: T=14.6°C, pale olive (10Y 6/2), clay, FeOOH
225 cm; End of core